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SURVEY REPORTS ON ATMOSPHERIC EMISSIONS FROM THE PETROCHEMICAL INDUSTRY, VOLUME II

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Air Products and Chemicals, Incorporated

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16. ABSTRACT

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry. A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in four volumes numbered EPA-450/3-73-005-a, -b, -c, and -d.

This volume covers the following processes: Carbon Disulfide, Cyclohexanone, Dimethyl Terephthalate and Terephthalic Acid, Ethylene, Ethylene Dichloride via Direct Chlorination, Formaldehyde Manufacture with Silver Catalyst, Glycerol, Hydrogen Cyanide, and Isocyanates. For each process the report includes a process description, a process emission inventory, a catalog of emission control equipment, a list of producers, and an evaluation of the significance of the air pollution from the process. Also included is a summary table of emissions to the atmosphere from all the processes studied.

PRICES SUBJECT TO CHANGE

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Ethylene	Petrochemical Industry	7A
Carbon Monoxide	Formaldehyde	Particulates	7B
Hydrocarbons	Glycerol	Dimethyl Terephthalate	7C
Nitrogen Dioxide	Hydrogen Cyanide	Terephthalic Acid	13B
Sulfur Dioxide	Isocyanates	Ethylene Dichloride	13H
Carbon Disulfide		1-2 Dichloroethane	
Cyclohexanones		Toluene Diisocyanate	

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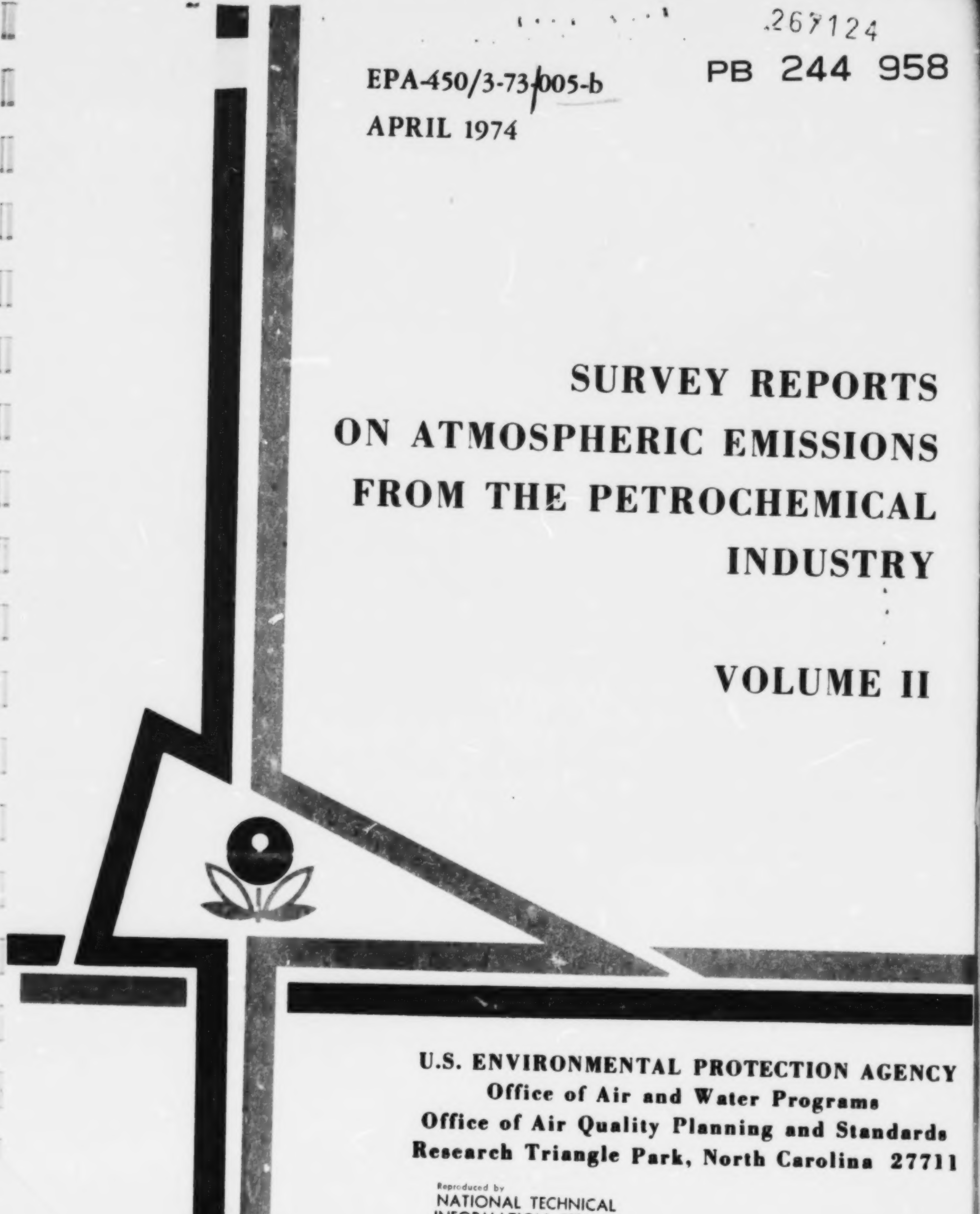

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VOLUME II

by

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry.

A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in these four volumes numbered EPA 450/3-73-005-a, -b, -c, and -d. The Tables of Contents of these reports list the processes that have been surveyed.

Those processes which have a significant impact on air quality are being studied in more detail by EPA. These in-depth studies will be published separately in a series of volumes entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a, -b, -c, etc.) At the time of this writing, a total of seven petrochemicals produced by 11 distinctly different processes has been selected for this type of study. Three of these processes, used to produce two chemicals (polyethylene and formaldehyde), were selected because the survey reports indicated further study was warranted. The other five chemicals (carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride and ethylene oxide) were selected on the basis of expert knowledge of the pollution potential of their production processes. One or more volumes in the report series will be devoted to each of these chemicals.

ACKNOWLEDGEMENTS

Survey and study work such as that described in this report have value only to the extent of the value of the imput data. Without the fullest cooperation of the companies involved in producing the petrochemicals that have been studied, this report would not have been possible. Air Products wishes to acknowledge this cooperation by commending:

The U. S. Petrochemical Industy
Member Companies of the Industry
The Manufacturing Chemists Association

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V	Number of New Plants (1973-1980)*

*Fifteen highest ranks from Table I.

NOTE: There are numerous tables and figures in the Survey Reports that are included in the appendicies of this report. These tables and figures are separately listed in each appendix.

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SUMMARY

A study of air pollution as caused by the petrochemical industry has been undertaken in order to provide data that the Environmental Protection Agency can use in the fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of the study includes most petrochemicals which fall into one or more of the classifications of (a) large production, (b) high growth rate, and (c) significant air pollution. The processes for the production of each of these selected chemicals have been studied and the emissions from each tabulated on the basis of data from and Industry Questionnaire. A survey report prepared for each process provides a method for ranking the significance of the air pollution from these processes. In-depth studies on those processes which are considered to be among the more significant polluters either have been or will be provided.

To date, drafts of in-depth studies on seven processes have been submitted. In addition, two further processes have been selected for in-depth study and work on these is in progress. All of these in-depth studies will be separately reported under Report Number EPA-450/3-73-006 a, b, c, etc.

A total of 33 Survey Reports have been completed and are reported here, or in one of the other three volumes of this report series.

I. Introduction

A study has been undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study is to provide data that are necessary to support the Clean Air Ammendments of 1970.

The information sought includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an industry questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

A method for rating the significance of air emissions was established and is used to rank the processes as they are studied. The goal of the ranking technique is to aid in the selection of candidates for in-depth study. These studies go beyond the types of information outlined above and include technical and economic information on "best systems" of emission reduction, the economic impact of these systems, deficiencies in petrochemical pollution control technology and potential research and development programs to overcome these deficiencies. These studies also recommend specific plants for source testing and present suggested checklists for inspectors.

This final report presents a description of the industry surveys that have been completed, as well as a status summary of work on the in-depth studies.

The Appendicies of this report include each of the 33 Survey Reports that were prepared during the course of the study.

II. Discussion

A. Petrochemicals to be Studied

There are more than 200 different petrochemicals in current production in the United States. Many of these are produced by two or more processes that are substantially different both with respect to process techniques and nature of air emissions. Although it may eventually become necessary to study all of these, it is obvious that the immediate need is to study the largest tonnage, fastest growth processes that produce the most pollution.

Recognizing this immediate need, a committee of Air Products' employees and consultants reviewed the entire list of chemicals and prepared a list of thirty chemicals which were recommended for primary consideration in the study and an additional list of fourteen chemicals that should receive secondary consideration. Since this was only a qualitative evaluation it was modified slightly as additional information was received and after consultation with the Environmental Protection Agency (EPA).

The final modified list of chemicals to be studied included all but three from the original primary recommendations. In addition, four chemicals were added and one was broken into two categories (namely low and high density polyethylene) because of distinct differences in the nature of the final products. This resulted in thirty-two chemicals for study and fourty one processes which are sufficiently different to warrant separate consideration. Hence, the following list of petrochemicals is the subject of this study.

Acetaldehyde (2 processes)
Acetic Acid (3 processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (2 processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (2 processes)
Ethylene Oxide (2 processes)
Formaldehyde (2 processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (2 processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (2 processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

B. Preliminary Investigations

Immediately upon completion of the preliminary study lists, a literature review was begun on those chemicals which were considered likely candidates for study. The purpose of the review was to prepare an informal "Process Portfolio" for each chemical. Included in the portfolio are data concerning processes for producing the chemical, estimates of growth in production, estimates of production costs, names, locations and published capacities of producers, approximations of overall plant material balances and any available data on emissions or their control as related to the specific process.

The fundamental purpose of these literature reviews was to obtain background knowledge to supplement what was ultimately to be learned from completed Industry Questionnaires. A second and very important purpose was to determine plant locations and names of companies producing each chemical. This information was then used to contact responsible individuals in each organization (usually by telephone) to obtain the name and address of the person to whom the Industry Questionnaire should be directed. It is believed that this approach greatly expedited the completion of questionnaires. The mailing list that was used is included as Appendix I of this report.

C. Industry Questionnaire

Soon after the initiation of the petrochemical pollution study, a draft questionnaire was submitted by Air Products to the Environmental Protection Agency. It had been decided that completion of this questionnaire by industry would provide much of the information necessary to the performance of the study. The nature and format of each question was reviewed by EPA engineers and discussed with Air Products engineers to arrive at a modified version of the originally proposed questionnaire.

The modified questionnaire was then submitted to and discussed with an Industry Advisory Committee (IAC) to obtain a final version for submission to the Office of Management and Budget (OMB) for final approval, as required prior to any U. S. Government survey of national industries. The following listed organizations, in addition to the EPA and Air Products, were represented at the IAC meeting:

Trade Associations

Industrial Gas Cleaning Institute
Manufacturing Chemists Association

Petrochemical Producers

B. F. Goodrich Chemical Company
E. I. duPont deNemours and Company
Exxon Chemical Company
FMC Corporation
Monsanto Company
Northern Petrochemical Company
Shell Chemical Company
Tenneco Chemicals, Inc.
Union Carbide Corporation

Manufacturers of Pollution Control Devices

John Zink Company
UOP Air Correction Division

State Pollution Control Departments

New Jersey
Texas

The questionnaire, along with a detailed instruction sheet and an example questionnaire (which had been completed by Air Products for a fictitious process that was "invented" for this purpose) were submitted to the OMB for approval. In due course, approval was received and OMB Approval Number 158-S-72019 was assigned to the questionnaire. Copies of the approved instruction sheet, example questionnaire are included as Appendix II of this report.

The questionnaires were mailed in accordance with the mailing list already discussed and with a cover letter that had been prepared and signed by the EPA Project Officer. The cover letter was typed in a manner that permitted the insertion of the name and address of the receipient at the top of the first page and the name of the process, the plant location and an expected return date at the bottom of the first page. A copy of this letter of transmittal is also included in Appendix II.

Understandably, because of the dynamic nature of the petrochemical industry, about 10 percent of the questionnaires were directed to plants which were no longer in operation, were still under construction, were out-of-date processes or were too small to be considered as typical. This did not present a serious problem in most cases because (a) 100 percent of the plants were not surveyed and (b) the project timing permitted a second mailing when necessary. Appendix III tabulates the number of questionnaires incorporated into each study.

One questionnaire problem that has not been resolved is confidentiality. Some respondents omitted information that they consider to be proprietary. Others followed instructions by giving the data but then marked the sheet (or questionnaire) "Confidential". The EPA is presently trying to resolve this problem, but until they do the data will be unavailable for inclusion in any Air Products' reports.

D. Screening Studies

Completed questionnaires were returned by the various respondents to the EPA's Project Officer, Mr. L. B. Evans. After reviewing them for confidentiality, he forwarded the non-confidential data to Air Products. These data form the basis for what has been named a "Survey Report". The purpose of the survey reports being to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". These reports are included as appendicies to this report.

Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for calculating a Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix IV of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emissions Summary Table that constitutes part of this report. This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes being studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process (Block) flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were established for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) are proposed.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR are proposed.

The bases for these ratings and example calculations are included in Appendix V of this report.

E. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furance Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional processes be "nominated" for in-depth study. The chemicals involved are phthalic anhydride, formaldehyde and ethylene oxide. Work on these indicated a need for four additional in-depth studies as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst.

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

Drafts of these have been submitted to the EPA and reviewed by the Industry Advisory Committee. The phthalic anhydride report also includes a section on production from naphthalene by air oxidation, a process which is considered to be a significant polluter in today's environment but without significant growth potential.

These seven in-depth studies will be separately issued in final report form, under Report Number EPA-450/3-73-006 a, b, c, etc.

An in-depth study, besides containing all the elements of the screening studies, delves into questions such as "What are the best demonstrated systems for emission reduction?", "What is the economic impact of emission control on the industry involved?", "What deficiencies exist in sampling, analytical and control technology for the industry involved?".

In striving to obtain answers to these questions, the reports include data on the cost effectiveness of the various pollution control techniques source testing recommendations, industry growth projections, inspection procedures and checklists, model plant studies of the processes and descriptions of research and development programs that could lead to emission reductions.

Much of the information required to answer these questions came from the completed Industry Questionnaires and the Process Portfolios. However, the depth of understanding that is required in the preparation of such a document can only be obtained through direct contact with the companies that are involved in the operation of the processes being studied. Three methods for making this contact were available to Air Products. The first two are self-evident, as follows: Each questionnaire contains the name, address and telephone number of an individual who can provide additional information. By speaking with him, further insight was obtained into the pollution control problems that are specific to the process being studied; or through him, a visit to an operating plant was sometimes arranged, thus achieving a degree of first hand knowledge.

However, it was felt that these two techniques might fall short of the level of knowledge desired. Thus, a third, and unique procedure was arranged. The Manufacturing Chemists Association (MCA) set up, through its Air Quality Committee (AQC), a Coordinating Technical Group (CTG) for each in-depth process. The role of each CTG was to:

1. Assist in the obtaining of answers to specific questions.

2. Provide a review and commentary (without veto power) on drafts of reports.

The AQC named one committee member to provide liaison. In several cases, he is also one of the industry's specialists for the process in question. If not, one other individual was named to provide CTG leadership. Coordination of CTG activities was provided by Mr. Howard Guest of Union Carbide Corporation who is also on the EPA's Industry Advisory Committee as the MCA Representative. CTG leadership is as follows:

Chemical	AQC Member	Other
Carbon Black	C. B. Beck Cabot Corporation	None
Acrylonitrile	W. R. Chalker Du Pont	R. E. Farrell Sohio
Formaldehyde	W. B. Barton Borden	None
Ethylene Dichloride	W. F. Bixby B. F. Goodrich	None
Phthalic Anhydride	E. P. Wheeler Monsanto	Paul Hodges Monsanto
Ethylene Oxide	H. R. Guest Union Carbide	H. D. Coombs Union Carbide

F. Current Status

Survey Reports on each of the 33 processes that were selected for this type of study have been completed, following review of the drafts by both the EPA and the Petrochemical Industry. These reports constitute the subject matter of this report.

In-depth studies of the seven processes mentioned above have been completed in draft form, submitted to the EPA for initial review, discussed in a public meeting with the Industry Advisory Committee and re-submitted to the EPA in revised form. They are currently receiving final EPA review and will be issued as final reports, following that review.

The EPA has now selected two additional processes for in-depth study and work on these is currently in progress. They are:

1. High Density Polyethylene via the Low and Intermediate Pressure Polymerization of Ethylene.

2. Low Density Polyethylene via the High Pressure Polymerization of Ethylene.

III. Results

The nature of this project is such that it is not possible to report any "results" in accordance with the usual meaning of the word. Obviously, the results are the Survey Reports and In-Depth Studies that have been prepared. However, a tabulation of the emission data collected in the study and summarized in each of these reports will be useful to the EPA in the selection of those processes which will be either studied in-depth at some future date, or selected for the preparation of new source standards. Such a tabulation, entitled "Emissions Summary Table", is attached.

IV. Conclusions

As was stated above under "Results", the conclusions reached are specific to each study and, hence, are given in the individual reports. Ultimately, some conclusions are reachable relative to decisions on processes which require future in-depth studies or processes which warrant the promulgation of new source standards.

A firm basis for selecting these processes is difficult to achieve, but the data contained in the Emissions Summary Table can be of value in setting a basis, or selecting processes.

It is imperative, when using the table, to be aware of the following facts.

1. The data for some processes are based on 100 percent survey of the industry, while others are based on less than 100 percent with some as few as a single questionnaire.
2. Some of the reported data are based on stack sampling, others on continuous monitoring and still others on the "best estimate" by the person responsible for the questionnaire.
3. Air Products attempted to use sound engineering judgement in obtaining emission factors, industry capacities and growth projections. However, other engineering firms, using the same degree of diligence would undoubtedly arrive at somewhat different final values.

Thus, the tabulation should be used as a guide but not as a rigorous comparison of process emissions.

Furthermore, data on toxicity of emissions, odors and persistence of emitted compounds are not included in the tabulation. In addition, great care must be used when evaluating the weighted emission rates because of the wide range in noxiousness of the materials lumped together in the two most heavily weighted categories. For example, "hydrocarbons" includes both ethane and formaldehyde and "particulates" includes both phthalic anhydride and the permanent hardness of incinerated water.

Bearing all of these qualifications in mind, several "top 15" rankings of processes can be made, as in Tables II through V. Obviously, one of these tables could be used to select the more significant polluters directly. Of course, other rankings could be made, such as leading emitters of NO_x or particulates, etc. Using these four tables, however, one analysis might be that the number of times a process appears in these tables is a measure of its pollution significance, or in summary:

Appear in 4 Tables

- Carbon Black
- Low Density Polyethylene
- High Density Polyethylene
- Cyclohexanone
- Polypropylene
- Polyvinyl Chloride
- Ethylene Oxide

Appear in 3 Tables

- Acrylonitrile
- Adiponitrile (Butadiene)
- Ethylene Dichloride (Oxychlorination)
- Dimethyl Terephthalate
- Ethylene Dichloride (Direct)
- Ethylene

Appear in 2 Tables

Maleic Anhydride
Isocyanates
Phenol
Formaldehyde (Silver)

Appear in 1 Table

Phthalic Anhydride
Formaldehyde (Iron Oxide)
Polystyrene
Nylon 6
Nylon 6,6
Vinyl Chloride

Thus, on this basis and in retrospect, it could be concluded that four of the selected in-depth studies (carbon black, ethylene oxide, and both low and high density polyethylene) were justified but that three of them (phthalic anhydride and both formaldehyde processes) were of lesser importance.

On the same basis, seven processes should be considered for future in-depth studies, namely:

Cyclohexanone
Polypropylene
Polyvinyl Chloride
Adiponitrile (Butadiene Process)
Dimethyl Terephthalate (and TPA)
Ethylene Dichloride (Direct)
Ethylene

Obviously, many alternative bases could be established. It is not the function of this report to select a basis for initiating future studies because the priorities of the EPA are unknown. The most apparent of these bases are the ones suggested by Tables II through V, namely the worst total polluters, the worst polluters on a weighted basis, the greatest increase in pollution (total or weighted) or the largest numbers of new plants. In addition, noxiousness of the emissions (photo-chemical reactivity, toxicity, odor, persistence) could be considered in making a selection.

TABLE 1
EMISSIONS SUMMARY

Page 1 of 3

ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.14	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE 1
EMISSION SUMMARY

ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS./YEAR

	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

Page 3 of 3

	Emissions (2), MM lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	466	966
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	1	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	11	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

TABLE II

TOTAL ANNUAL EMISSIONS, ALL "POLLUTANTS", BY 1980 (MM LBS./YR.)*

Carbon Black	5,730
Acrylonitrile	980
Maleic Anhydride	566
Low Density Polyethylene	343
Cyclohexanone	310
High Density Polyethylene	297
Dimethyl Terephthalate	265
Ethylene Dichloride	253
Phthalic Anhydride (Total)	233
Formaldehyde (Silver)	212
Polypropylene	190
Isocyanates	175
Polyvinyl Chloride	137
Adiponitrile (Butadiene Process)	129
Ethylene Oxide	120

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE III

TOTAL ANNUAL WEIGHTED EMISSIONS BY 1980 (MM LBS./YR.)*

Acrylonitrile	38,000
Low Density Polyethylene	27,400
Carbon Black	24,740
High Density Polyethylene	23,600
Ethylene Dichloride (Oxychlorination)	16,450
Polypropylene	15,140
Dimethyl Terephthalate	13,500
Cyclohexanone	11,960
Polyvinyl Chloride	10,540
Ethylene Oxide	9,530
Adiponitrile (Butadiene Process)	6,210
Maleic Anhydride	5,670
Ethylene Dichloride (Direct)	5,040
Ethylene	3,670
Phenol	3,640

*Fifteen highest numbers, as summarized in Table I, for this category.

TABLE IV

SIGNIFICANT EMISSION INDEX*

Acrylonitrile	23,000
Low Density Polyethylene	21,300
High Density Polyethylene	17,200
Polypropylene	12,190
Ethylene Dichloride (Oxychlorination)	8,800
Carbon Black	7,200
Cyclohexanone	6,260
Dimethyl Terephthalate	6,040
Polyvinyl Chloride	4,840
Adiponitrile (Butadiene)	3,010
Ethylene Dichloride (Direct)	2,740
Maleic Anhydride	2,720
Ethylene Oxide	2,650
Ethylene	2,430
Vinyl Chloride	2,170

*Fifteen higest numbers, as summarized in Table I, for this category.

TABLE V

NUMBER OF NEW PLANTS (1973-1980)*

Low Density Polyethylene	41
Formaldehyde (Silver)	40
Polypropylene	32
High Density Polyethylene	31
Polyvinyl Chloride	25
Polystyrene	23
Ethylene	21
Ethylene Oxide	15
Carbon Black	13
Formaldehyde (Iron Oxide)	12
Phenol	11
Cyclohexanone	10
Isocyanates	10
Nylon 6	10
Nylon 6,6	10
Ethylene Dichloride (Direct)	10

*Fifteen highest numbers, as summarized in Table I, for this category.

Carbon Disulfide

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I. Introduction

Carbon disulfide is a colorless and extremely volatile and flammable liquid. It is the basic raw material in the production of viscose rayon, cellophane, carbon tetrachloride and certain pesticides and fungicides. The compound was first synthesized 200 years ago. Up until the early 1950's all commercial production was based upon the reaction of charcoal with sulfur. Today, all carbon disulfide manufactured in the U. S. is produced using methane feed. Alternate feed stocks including fuel oils and petroleum coke are currently being investigated and may be a major raw material source for carbon disulfide in the future.

U. S. capacity, at present, stands at 871 MM lbs./year. Growth is expected to be around 3% a year and capacity by 1980 should be in the neighborhood of 1.1 billion lbs./year.

Emissions from carbon disulfide production are primarily associated with the Claus plant used to recover sulfur. Emissions from Calus processes are not within the scope-of-work for this project and will not be discussed here. Other sources of emissions are: boiler flue gas, emergency flare flue gas and storage leaks. Emissions from a carbon disulfide plant, excluding the Claus plant, are low in comparison to other processes currently being surveyed. Emissions from plants using fuel oil or coke as feed should be comparable to that of the methane process because of the vast similarities between the two processes.

II. Process Description

Carbon disulfide is produced by the catalytic reaction of methane with sulfur vapor.

$$CH_4 + 2\,S_2 \longrightarrow CS_2 + 2\,H_2S$$

Thermodynamically, the reaction is very favorable for carbon disulfide formation with yields of over 90% per pass being typical. The reaction of methane with diatomic sulfur vapor is exothermic. However, vapor phase dissociation of the octatomic molecule formed when sulfur is first vaporized to the diatomic and hexatomic forms which predominate at higher temperatures requires heat. The overall process is endothermic and care must be taken to dissociate as many of the octatomic molecules as possible in the superheater in order to limit the temperature drop across the adiabatic reactor.

Liquid sulfur, which is maintained at about 130° C is transferred to a boiler where it is vaporized and heated to 575 - 650° C in order to convert sulfur largely to the diatomic form. Methane is preheated to 550 - 650° C and mixed with the sulfur vapors. The mixed vapors, with sulfur in 10% excess of stoichiometric requirements, are fed into the reactor or reactors. Two types of catalytic reactor system are employed commercially. In the first, preheated feed at about 675° C is fed to a single fixed bed adiabatic reactor with a silica gel catalyst. The other employs two fixed bed adabatic reactors with reheating in between. The feed enters each reactor at about 600° C. In either case, typical yields are from 90 - 95%.

The reactor effluent is cooled to approximately 130° C and unreacted sulfur is separated in a gas-sulfur separator. Sulfur dust is recovered by scrubbing with liquid sulfur. The carbon disulfide is separated from the hydrogen sulfide by preferential absorbtion in mineral oil from which it is subsequently stripped and sent to the distillation section. Hydrogen sulfide gas is usually sent to a Claus plant where sulfur is recovered and recycled. Carbon disulfide is separated from impurities in two distillation columns. In the first, low boiling impurities are removed overhead. In the second, high boiling impurities are removed in the bottoms and carbon disulfide product is produced overhead.

III. Plant Emissions

A. Continuous Air Emissions

1. Furnace Flue Gas

Natural gas is usually burned to supply the heat necessary to heat and superheat the reactants to the required temperature. Respondent 8-3 calculated the amount of pollutants produced by using EPA Emission Factor Rating B for Natural Gas Combustion. He reports .00004 lbs. of particulate per pound of CS_2; .00014 lbs. of NO_x per lb. CS_2 and .00009 lbs. of hydrocarbons per lb. CS_2.

2. Liquid Waste Incineration

One plant, 8-3 utilized a thermal oxidizer to burn heavy waste produced by the process along with tail gas from their Claus plant. Since three-fourths of the liquid is carbon disulfide and dissolved sulfur, substantial amounts of sulfur dixoide (.00662 lbs./lb. CS_2) are produced from this source.

3. Sulfur Pit and Storage Losses

Approximately .00028 lbs. of sublimated sulfur per lb. CS_2 are released to the atmosphere through losses in the sulfur pit area and storage tank vents.

4. Carbon Disulfide Storage Losses

Because carbon disulfide autoignites at 100° C storage losses are kept to the minimum. Usually the product is stored under water and losses are negligible.

B. Intermittent Air Emissions

1. Emergency Flares

All emergency venting, due to utility failure, compressor failure, start-up and shutdown, etc. in carbon disulfide plants, is done through flares. Since sulfur is present in almost all compounds used or porudced in the process extremely high sulfur dioxide emissions will result for a short period of time. Respondent 8-5 reports that 4.6 tons/month of sulfur containing compounds are burned through the emergency flare. Other plants report smaller but still substantial emergency emissions.

C. Continuous Liquid Wastes

The quantity of waste water produced by the process and the method used to treat the waste is summarized below for the plants surveyed.

EPA Code No.	GPM	Treatment
8-1	30	On-site
8-3	20	On-site
8-4	12	On-site
8-5	0	

D. Solid Wastes

Only plant 8-3 reports any solid wastes produced by the process. 25 lbs./day of oily sludge are disposed of in an undisclosed manner.

E. Odor

None of the respondents reported any odors associated with the process, however, during emergency conditions large amounts of sulfur dioxide are released to the atmosphere, and in spite of high temperatures and tall stacks, it is possible that an odor could be released to the surrounding area.

F. Fugitive Emissions

Fugitive emissions due to leaks, spills are estimated to be .00007 lbs./lb. CS_2.

IV. Emission Control

The emission control devices that have been reported as being employed by carbon disulfide producers are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been made available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{(\text{pollutant x weighting factor}^{*})\text{in} - (\text{pollutant x weighting factor})\text{out}}{(\text{pollutant x weighting factor})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor

Normally, a combustion type control device (i.e., incinerator, flare, etc.) will be assigned a "CCR" and a "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V.

Flares

All carbon disulfide plants have flares to burn the components of streams that are vented to the atmosphere in case of an emergency or shutdown. Unfortunately since the streams flared usually consists of sulfur compounds, including hydrogen sulfide, carbon disulfide, carbonyl sulfide and sulfur, the net effect is to replace one harmful polluant with another. Since the "SERR" efficiency is designed to weight this effect it has been calculated wherever possible. Efficiencies of 53% and 18% have been calculated for flares FL-V and FL-II, respectively.

Incineration

Thermal oxidizer IN-I is listed in Table IV even though it contributes to air pollution, because it serves the purpose of destroying harmful liquid waste. It would be ludicrous to assign an efficiency to this device. It is also rather doubtful that this is the best way to dispose of highly sulfurous waste.

V. Significance of Pollution

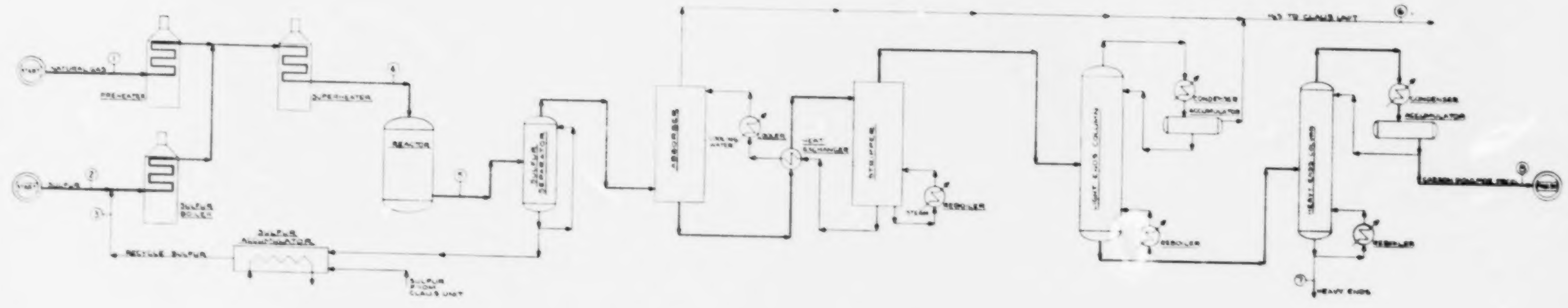
It is recommended that no in-depth study of this process be undertaken at this time. The most significant source of air pollution associated with the production of carbon disulfide is emissions from the Claus plant used to recover sulfur. Emissions from the Claus process are not covered in this report. Air pollutants released as air emissions, for the process under study are less than for other processes currently being surveyed.

The methods outlined in Appendix IV have been used to estimate the total weighted annual emissions from new plants which will be in operation by 1980. The work is summarized in Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index of 30 has been calculated in Table VII. This is substantially less than the SEI's of other processes in the study. Hence, the recommendation to exclude carbon disulfide from the in-depth portion of the overall scope of work.

VI. Carbon Disulfide Producers

Company	Location	Capacity - MM Lbs./Year
FMC - Allied	South Charleston, W. Va.	220
Pennwalt	Houston, Texas	10
PPG	New Martinsville, W. Va.	53
Stauffer	Delaware City, Del.	350
Stauffer	LeMoyne, Ala.	238
		Total - 871


START
NATURAL GAS
①
PREHEATER
START
SULFUR
②
③
SULFUR BOILER
SUPERHEATER
④
REACTOR
⑤
SULFUR SEPARATOR
SULFUR ACCUMULATOR
RECYCLE SULFUR
SULFUR FROM CLAUS UNIT
ABSORBER
COOLING WATER
COOLER
HEAT EXCHANGER
STRIPPER
STEAM
REBOILER
LIGHT ENDS COLUMN
CONDENSER
ACCUMULATOR
REBOILER
H2S TO CLAUS UNIT
⑥
HEAVY ENDS COLUMN
CONDENSER
ACCUMULATOR
REBOILER
⑦
HEAVY ENDS
CARBON DISULFIDE PRODUCT
⑧
END

NOTES:
NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES TO MATERIAL BALANCE TABLE I

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT [illegible]
FIGURE [illegible]
SIMPLIFIED FLOW DIAGRAM
CARBON DISULFIDE [illegible]
NONE
TTKA
408
R-235
A

TABLE CD-I

MATERIAL BALANCE

CARBON DISULFIDE FROM
METHANE & SULFUR

COMPONENT	Stream No. Stream	1 & 2 Fresh Feed	3 Recycle Sulfur	4 Total Feed	5 Reactor Effluent	6 Gas to Claus Unit	7 Heavy Ends	8 Product
Natural Gas								
1) Methane		.2493		.2493	.0347	.0347		
2) Ethane		.0071		.0071	.0030	.0030		
3) Propane		.0020		.0020	.0013	.0013		
4) O_2, N_2, CO_2		.0046		.0046				
Sulfur		.9051	.9690(1)	1.8741	.1717			
Carbon Disulfide					1.0116	.0116		1.0000
Hydrogen Sulfide					8967	.8967		
Carbonyl Sulfide					.0078	.0078		
Hydrogen					.0078	.0078		
Nitrogen					.0008	.0008		
Heavy Products								
Sulfur, Oil, Etc.					.0017		.0017	
		1.1681	.9690	2.1371	2.1371	.9637	.0017	1.0000

(1) Includes sulfur recovered from Claus unit.

TABLE CD-II
HEAT BALANCE (REACTOR SECTION ONLY)
CARBON DISULFIDE FROM METHANE AND SULFUR

Heat In (1)	
Heat, vaporization and superheat for sulfur and methane (above base temperature)	755
Exothermic heat of reaction	324
	1,079 BTU/LB. CS_2
Heat Out	
Endothermic heat of dissociation for S_8	568
Enthalpy residual (above base temperature)	511
	1,079 BTU/LB. CS_2

(1) Base temperature - 130° C (inlet temperature to boiler for liquid sulfur).

TABLE CD-III

NATIONAL EMISSIONS INVENTORY

CARBON DISULFIDE FROM METHANE AND SULFUR

Page 1 of 4

E.P.A. CODE NO. 8-1

CAPACITY TONS OF CARBON DISULFIDE Approx. 5,000 (1)

AVERAGE PRODUCTION - TONS OF CARBON DISULFIDE (1)

EMISSIONS TO ATMOSPHERE

Steam	Fumes From Sulfur Pit	Sulfur Storage Vent	Flue Gas From Start-Up Flare	Flare Flue Gas Emergency Reactor Vent	Storage Loss (4)
Flow-Lbs./Yr.	Not Specified	Not Specified	Not Specified	18,562	
Flow Characteristics - Continuous or Intermittent	Continuous	Continuous	Intermittent	Intermittent	
If Intermittent - Hrs./Yr.			50	.66	
Composition Lbs./Hr. of Component					
Methane					+
Ethane					
Propane					
Sulfur	+	+			
Carbonyl Sulfide		+			
Carbon Disulfide					+
Theophene					
Hydrogen Sulfide		+			
Sulfur Dioxide				14,041	
Nitrogen			+	0.5	
Nitrogen Dioxides			+		
Carbon Dioxide		+	+	2,486	
Oxygen			+		
Water			+	2,035	
Hydrocarbons		+			
Analysis	None	None	None	None	None
Date of Frequency of Sampling					
Type of Analysis					
Odor Problem	No	No	Yes	Yes	No
Vent Stacks	No	Yes	Yes	Yes	Yes
Flow SCFM Per Stack				60 - 2000	0 - 12
Number		1	1	1	1
Height (Elev. @ tip) - Ft.		30	12	150	30
Diameter - Inches		3	2	8	2
Exit Gas Temperature - F^{o}		250	1200	3000	Ambient
Emission Control Devices	No	No			No
Type - Scrubber					
- Incinerator - Flare			Yes	Yes	
Summary of Pollutants					
Hydrocarbons Lbs./Hr. + Other Sulfur Compounds Besides SO_x		+			+
Particulates	+ (3)				
NO_x - Lbs./Hr.			+	0.5	
SO_x - Lbs./Hr.				14,041	
CO - Lbs./Hr.					

(1) Exact capacity and production figures are confidential

(2) Since capacity is calssified information it is not possible to represent composition in the usual manner of tons/tons product.

(3) Sublimed sulfur.

(4) Average of 3.7 SCFM.

TABLE CD-III

NATIONAL EMISSIONS INVENTORY

CARBON DISULFIDE
FROM METHANE AND SULFUR

Page 2 of 4

EPA CODE NO.	8-3			
CAPACITY TONS OF CARBON DISULFIDE	119,000			
AVERAGE PRODUCTION - TONS OF CARBON DISULFIDE	119,000			

EMISSIONS TO ATMOSPHERE	**Boiler Flue** Gas	Flue Gas - Liquid **Waste** Incineration	Flue Gas Emergency Flare	**Storage Loss**
Steam				
Flow Lbs/Yr.	24,605	(1)	Not Specified	20
Flow Characteristics - Continuous or Intermittent	Continuous	Continuous	Intermittent	Continuous
If Intermittent - Hrs./Yr.			1	
Composition Tons/Ton of Carbon Disulfide				
Particulates	.00004			
Methane				
Ethane				
Propane				
Sulfur				
Carbonyl Sulfide				
Carbon Disulfide				Negligible
Theophene				
Hydrogen Sulfide				
Sulfur Dioxides	Negligible	.00662 (3)	+	
Nitrogen				
Nitrogen Dioxides	.00014	+	+	
Carbon Monoxide	Negligible			
Carbon Dioxide	.46342	(1)	+	
Water	.37918	(1)		
Hydrocarbons	.00009			Negligible
Analysis	None	Yes	None	None
Date of Frequency of Sampling		Once/Month		
Type of Analysis	Calc'd.	Chromatagraph		
Odor Problem	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow SCFM Per Stack	Not Specified			70
Number	1	1		
Height (Elev. @ tip.) - Ft.	100	150		35-50
Diameter - Inches	50	78		36
Exit Gas Temperatures - F^{o}	800	1000		Ambient
Emission Control Devices	No	Yes	No	No
Type - Scrubber				
Incinerator - Flare		Yes (2)	Yes	
Summary of Pollutants				
Hydrocarbons + Sulfur Containing Compounds besides SO$_x$ - Tons/Ton Carbon Disulfide	.00009	0	0	Negligible
Particulates - Tons/Ton Carbon Disulfide	.00004	0	0	0
NO$_x$ - Tons/Ton Carbon Disulfide	.00014	+	+	0
SO$_x$ - Tons/Ton Carbon Disulfide	Negligible	.00662	+	0
CO - Tons/Ton Carbon Disulfide	Negligible	0	0	0

(1) Not enough information to calculate - Incinerator bufns claus tail gas also.
(2) Converts harmful liquid waste to air pollutants
(3) SO$_2$ from liquid waste only.

TABLE CD-III

NATIONAL EMISSIONS INVENTORY

CARBON DISULFIDE FROM
METHANE AND SULFUR

Page 3 of 4

EPA CODE NO. 8-4

CAPACITY TONS OF CARBON DISULFIDE 175,000

AVERAGE PRODUCTION - TONS OF CARBON DISULFIDE 175,000

EMISSIONS TO ATMOSPHERE

Stream	Boiler Flue Gas	Reactor Emergency Vent Flare	Emergency Storage Tank Vent
Flow-Lbs./Hr.	13,221	20,800	47
Flow Characteristics - Continuous or Intermittent	Continuous	Intermittent	Intermittent
If Intermittent - Hrs./Yr.		72	12
Composition Tons/Ton of Carbon Disulfide			
Methane			
Ethane			
Propane			
Sulfur			
Carbonyl Sulfide			
Carbon Disulfide			Negligible
Thiophene			
Hydrogen Sulfide			
Sulfur Dioxide		.00025	
Nitrogen			
Nitrogen Dioxides	.00001		Negligible
Carbon Dioxide	.29025	.00369	
Water	.23750		
Analysis	Not Specified	Yes	None
Date of Frequency of Sampling		Once	
Type of Analysis		Chromatagraph	
Ordor Problem	No	Yes	No
Vent Stacks	Not Specified	Yes	No
Flow SCFM per Stack			
Number		1	
Height (elev. @ tip) - Ft.		88	
Diameter - Inches		18	
Exit Gas Temperature - F^o		200	
Emission Control Devices	No	Yes	No
Type - Scrubber			
Incinerator - Flare		Yes	
Summary of Pollutants			
Hydrocarbons + Compounds Containing Sulfur besides SO_x - Tons/Ton Carbon Disulfide	0	0	Negligible
Particulates - Tons/Ton Carbon Disulfide	0	0	0
NO_x - Tons/Ton Carbon Disulfide	.00001	0	0
SO_x - Tons/Ton Carbon Disulfide	0	.00025	0
CO - Tons/Ton Carbon Disulfide	0	0	0

TABLE CD-III

NATIONAL EMISSIONS INVENTORY

CARBON DISULFIDE FROM
METHANE AND SULFUR

Page 4 of 4

EPA CODE NO. 8-5

CAPACITY TONS OF CARBON DISULFIDE 26,500

AVERAGE PRODUCTION - TONS OF CARBON DISULFIDE 26,500

EMISSIONS TO ATMOSPHERE

Stream	Sulfur Storage Vent	Flue Gas Emergency Flare	Storage Vent	Fugitive Emissions
Flow-Lbs./Hr.	1.7	33.758	0	.42
Flow Characteristics - Continuous or Intermittent	Continuous	Intermittent	Continuous	Continuous
If Intermittent - Hrs./Yr.		30		
Composition Tons/Ton of Carbon Disulfide				
Methane				
Ethane				
Propane				
Sulfur	.00028			
Carbonyl Sulfide				( )
Carbon Disulfide			Negligible	(.00007)
Thiophene				( )
Hydrogen Sulfide				
Sulfur Dioxide		.00478		
Nitrogen		.01260		
Nitrogen Dioxides				
Carbon Dioxide		.00005		
Water		.00122	Negligible	
Oxygen		.00685		
Analysis	None	None	None	None
Date of Frequency of Sampling				
Type of Analysis	Calc'd.	Calc'd.		
Ordor Problem	No	No	No	No
Vent Stacks	No	Yes	No	No
Flow SCFM per Stack		6780		
Number		1		
Height (elev. @ tip) - Ft.		110		
Diameter - Inches		12		
Exit Gas Temperature - F^o		1800		
Emission Control Devices	No	Yes	No	No
Type - Scrubber				
Incinerator - Flare		Yes		
Summary of Pollutants				
Hydrocarbons x Sulfur Contain Compounds besides SO_x - Tons/Ton Carbon Disulfide	0	0	Negligible	.00007
Particulates - Tons/Ton Carbon Disulfide	.00028	0	0	0
NO_x - Tons/Ton Carbon Disulfide	0	0	0	0
SO_x - Tons/Ton Carbon Disulfide	0	.00478	0	0
CO - Tons/Ton Carbon Disulfide	0	0	0	0

TABLE CD-IV

CATALOG OF EMISSION CONTROL DEVICES

CARBON DISULFIDE
FROM METHANE AND SULFUR

Page 1 of 2

Incineration Devices				
E.P.A. Code No. for Plant Using	8-1	8-1	8-3	8-3
Steam	Reactor Start Up Flare	Purification Sect. Emergy Flare	Purification Sect. Emergency Flare	Heavy Ends Thermal Oxidizer
Device I.D.	FL I	FL II	FL III	IN I
Type of Compound Incinerated	CS_2,H_2S,COS,Lt.HC	CS_2,H_2S,COS,Lt.HC	CS_2,H_2S,COS,Lt.HC	CS_2,S,Oil (1)
Type of Device - Flare	Yes	Yes	Yes	
Incinerator				
Other				Thermal Oxidizer
Material Incinerated (SCFM)	Not Specified	1050		143 lb./hr.
Auxiliary Fuel Required (Excl. Pilot)	↓	No	Yes	Yes (1)
Type	↓		Natural Gas	Natural Gas
Rate - BTU/Hr.	↓		125 SCFH	29,200 SCFH
Device or Stack Height - Ft.	↓	150	120	150
Installed Cost - Mat'l. & Labor - $	↓	10,000	135,000 20,000	250,000 75,000 25,000
Installed Cost Based on - "Year" - Dollars	↓	1967	1956 1969	1956 1967 1969
Installed Cost - c/Lb. of Carbon Disulfide	↓		.065	.15
Operating Cost - Annual - $(1972)	↓	1500	7500	105,000
Operating Cost - c/Lb. of Carbon Disulfide	↓		.003	.044
Efficiency - % - CCR	100%	100%	100%	100%
Efficiency - % - SERR	-	18%	-	Not Applicable (3)

(1) Devices also burns claus plant tail gas.

(2) Figures are for conbined function of incineration of liquid waste and claus plant tailgas.

(3) Since device converts harmful liquid waste to air pollution.

TABLE CD-IV

CATALOG OF EMISSION CONTROL DEVICES

CARBON DISULFIDE

FROM

METHANE & SULFUR

Incineration Devices			
E.P.A. Code No. for plant using		8-4	8-5
Steam		Purification Section Emergency Flare	Reactor & Purification Section Emergency Flare
Device I.D.		FL IV	FL-V
Type of compound incinerated		H_2S, CS_2, S_2	H_2S, CS_2, S_2, COS
Type of Device -	Flare	Yes	Yes
	Incinerator		
	Other		
Material Incinerated (SCFM)		Not Specified	500 - 700
Auxiliary	Fuel Required **(excl. pilot)**	↓	No
	Type	↓	
	Rate - Btu/Hr.	↓	
Device or Stack Height - Ft		↓	110
Installed Cost - Mat'l & Labor - $		↓	50,000
Installed Cost based on "year" - dollars		↓	1962
Installed Cost - c/lb of Carbon Disulfide		↓	.094
Operating Cost - Annual - $(1972)		↓	6600
Operating Cost - c/lb of Carbon Disulfide		↓	.012
Efficiency - % - CCR		100%	100%
Efficiency - % - SERR		-	53%

TABLE CD-V
NUMBER OF NEW PLANTS BY 1980

Current (1) Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
871	0	871	1,100 (2)	1,100 (3)	229	200	1-2

NOTE:

(1) MM lbs./year.

(2) 3% per year increase - Chem. Profile, April, 1970.

(3) MSA report for Environmental Protection Agency.

TABLE CD-VI
EMISSION SOURCE SUMMARY
T/T OF CARBON DISULFIDE

Emission	Source Furnace Flue Gas	 Sulfur Storage	 Emergency Flaring	 Fugitive Emissions	Total
Hydrocarbons*	.0009			.00007	00016
Particulates	.0004	.00028			.00032
NO_x	.00014				.00014
SO_x	Negligible		.00478		.00478
CO	Negligible				0

*Includes sulfur containing compounds excluding sulfur dioxides.

TABLE CD-VII
WEIGHTED EMISSION RATES

Chemical Carbon Disulfide

Process Methane

Increased Capacity 229 MM Lbs./Year

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons*	.00016	.0366	80	3
Particulates	.00032	.0732	60	4
NO_x	.00014	.0321	40	1
SO_x	.00478	1.09	20	22
CO	0		1	0

Significant Emission Index = 30

*Includes sulfur containing compounds excluding sulfur dioxides.

Cyclohexanone

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I. Introduction

Cyclohexanone is an important intermediate in the production of nylon 6 and nylon 6,6. It is produced, primarily, by the oxidation of cyclohexane; as is cyclohexanol, a chemical commonly produced in conjunction with cyclohexanone. Most of the tables and figures included in this report are keyed to the production of cyclohexanone - as the penultimate oxidation product of cyclohexane. However, as far as total emissions are concerned, it makes relatively little difference whether cyclohexanone or a mixture of cyclohexanone and cyclohexanol is produced.

Like most air oxidation processes, venting of the "spent air" accounts for the bulk of the 'emissions' associated with the production of cyclohexanone. The other prominent source of emissions is the distillation train with its attendant vent streams. Also the dehydrogenation section, where used, produces some emissions. In addition to the air emissions, quantities of waste organic acids and spent caustic are produced. In general, air emissions from the production of cyclohexanone could be characterized as moderate.

The current U. S. capacity for the production of cyclohexanone/cyclohexanol via the air oxidation of cyclohexane - including that material that is never separated, stored or traded as an item of commerce, i.e intermediates in the production of other chemicals (primarily adipic acid) - can be estimated at 1.8×10^9 lbs./yr. (1) By 1980 U. S. capacity for the production of cyclohexanone/cyclohexanol can be expected to double to 3.6×10^9 lbs./yr. There is no basis for forecasting a change in emission rate, i.e. tons emission/ton of cyclohexanone.

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(1) Based on Process Research Inc. estimate of current and future nylon capacity.

II. Process Description

The air oxidation of cyclohexane to cyclohexanol/cyclohexanone mixtures is carried out in the liquid phase. The conversion may be carried out thermally or catalytically. The latter approach predominates. (The pertinent chemical reactions are shown in Table I)

Either of two catalysts are normally used; a soluble salt of cobalt such as cobalt naphthanate or boric acid. Cobalt naphthanate is probably the more common catalyst. It is reportedly used in concentrations of 2 to 40 parts per million (on cyclohexane).

The use of boric acid as a 'catalyst' is a relatively recent innovation It is claimed that its use increases the reaction selectivity and raises the yield from 70% to about 90%. This is accomplished because yield loss is due primarily to the fact that oxidation does not stop at cyclohexanol or cyclohexanone, but proceeds to various oxidation products such as dicarboxylic acids. However, when the reaction is carried out in the presence of boric acid, cyclohexanol is tied up as an ester as soon as it is formed, thus precluding further oxidation. About .005 lbs. of boric acid per pound of cyclohexanone/cyclohexanol is consumed. Both I.F.P. and Scientific Design license boric acid processes.

The following description is based on a boric acid process: (see also Fig. I and Fig. II), Cyclohexane and a slurry of boric acid are pumped into a series of stirred autoclaves that are maintained at a temperature of about 300 ^{O}F and a pressure of about 200 PSIG. Air is compressed, and sparged into the bottom of each autoclave, where it initiates and sustains the oxidation reaction (Reaction I - Table I). The exothermic heat of reaction is removed by reflux condensers which are designed to (1) condense and return all hydrocarbons to the reactors, (2) reject water (which suppreses the oxidation) and (3) vent the "spent air" overhead. The liquid effluent from the final reactor is then mixed and washed with water. The water soluble compounds are separated, with the unreacted boric acid recycled and the other soluble acids rejected as an aqueous waste. The washed mixture of naphthene ketone, alcohol, ester and other reactants is then saponified to recover the esters formed by the reaction of the boric acid and cyclohexanol (Reaction II and III, Table I). The aqueous layer, containing soluble sodium salts, is rejected from the botton of a wash column. The washed hydrocarbon mixture is then pumped to the cyclohexane column where the unreacted cyclohexane is taken overhead and subsequently recycled to the oxidation reactors. The bottoms from the cyclohexane column are combined with the liquid effluent from the cyclohexanol dehydrogenation reactor and cyclohexanol from the cyclohexanol recovery unit. The combined stream is fractionated to reject heavy and light ends. The heart cut cyclohexanone/cyclohexanol mixture ("K-A Oil") may then be sent to intermediate storage prior to further processing (i.e. oxidation to adipic acid) or may be separated into its constituent components via the "one-ol" tower. The overhead product from the "one-ol" tower, cyclohexanone, is pumped to storage. The cyclohexanol bottoms are generally dehydrogenated to produce additional cyclohexanone.

III. Plant Emissions

A. Continuous Air Emissions

1. Oxidizer Vent

All cyclohexane air oxidation plants vent 'spent air' from the oxidizer/reactor. Generally this vent stream represents the single largest source of emissions in the plant. Within this general frame work there is still room for considerable variation in the magnitude of emissions reported for this source. The variations are primarily due to the amount of scrubbing done by the various respondents and whether or not air recycling techniques are utilized. All reported emissions are summarized in Table III.

2. Distillation Train Vents

Most of the emissions grouped under this heading are combustion products from the variety of devices used by the operators to combust the 'light ends' rejected by their distillation/purification facilities.

Also included are the emissions resulting from the operation of steam ejectors, as reported by the operators of EPA Coded Plants 9-1, 9-2 and 9-4. Operator 9-4 estimates losses from this source at 1-2% of production or about .015 lb./lb. This seems extremely high. Other emissions in this category are summarized in Table III.

3. Hydrogen Vent from Dehydrogenation Section

The three operators who indicated that they are dehydrogenating cyclohexanol all process this vent differently. The operator of plant 9-4 sends this stream to his boiler house, and thus reports no emissions. Operator of plant 9-2 removes condensibles by chilling, and then vents the non-condensibles. Operator 9-3 scrubs the stream prior to venting. The emissions reported by the latter two operators are summarized in Table III.

4. Plant Flares

Based on the sampling from the questionnaires about one half of the cyclohexanone/cyclohexanol plant operators utilize a continuously lighted plant flare or continuous service incineration device. The type of compounds normally burned in these devices should not result in the emission of significant amounts of pollutants. Minimal amounts of CO and NO_x can be expected during normal operation. Reported emissions are summarized in Table III.

5. Dehydrogenation Heater Flue Gas

Of the three operators reporting dehydrogenation operations (see Section III-A-3), all report using natural gas for heater fuel. Only one (9-2) reports sulfur content of the fuel - 4 ppm. At that concentration, SO_2 emissions from this source are entirely negligible. They amount to considerably less than .00001 ton/ton of cyclohexanone.

6. Storage Losses

Only about one half of the liquid storage tanks used by the respondents have vapor conservation devices. Consequently this emission source will contribute to the overall air pollution resulting from the operation of the subject process. It is imprudent to attempt to quantify this source without knowing further details about storage operations - i.e., tank configuration, storage temperature, average atmospheric conditions, etc. However, it is probably safe to say that relative to other cyclohexanone sources, the emissions are small.

B. Intermittent Air Emissions

No intermittent air emissions have been reported by cyclohexanone/cyclohexanol plant operators. However, atmosphere venting during start-ups and plant emergencies is an operation practiced universally by the petrochemical industry. Unfortunately, there is great variation in the rate and frequency of this type of emission and even an estimate (other than one from the industry) of the importance of this source relative to other tabulated sources would be imprudent.

C. Continuous Liquid Wastes

1. Waste Acid

Various organic acids are formed during the oxidation of cyclohexane. The water soluble acids are removed from the process by standard water washing techniques. Operators 9-2 and 9-3, both report similar flow rates for this aqueous waste stream - 10,000 lb./hr. and 14,000 lb./hr. respectively. Operator 5-4 indicates that this stream is neutralized, but he does not report the method of ultimate disposal. Operators 9-3 and 9-2 both report utilizing a combination of incineration and deep well injection methods as disposal techniques. Operator 5-3 uses deep well disposal.

2. Spent Caustic

The esters of cyclohexanol formed during the oxidation of cyclohexane are recovered by saponification. A spent caustic stream is generated by this procedure. Operators 9-3 and 9-2 report injecting 15,000 lb./hr. and 14,000 lb./hr. (respectively), of this material into deep wells. Presumably all operators must dispose of similar streams, but none report them.

3. Waste Water

Various quantities of waste water have been reported. They range from about 10 to 175 GPM. One operator (5-4) reports that his waste water stream contains 2.3 wt. % organics. However; that, is waste from an entire adipic acid plant; the amount produced by the cyclohexanone/cyclohexanol portion of the plant, if assumed to be half of the total, is 175 GPM of water containing 2,000 lb./hr. of organics.

D. Solid Wastes

Three operators (EPA Code No.'s. 5-4, 9-2 and 9-3) report the accumulation of from 120 to 250 lb./hr. of solid waste materials within their processing equipment. According to the latter two named respondents, this material is cleaned from the equipment once a year and used as in-plant land fill. Operator 5-4 does not report his disposal method.

E. Odors

In general, the air oxidation of cyclohexane to cyclohexanone/cyclohexanol does not appear to be a process that has an odor "problem".

Only one operator (EPA Code 9-3) reported an odor complaint in the last year. Most of the reported odors are said to be detectable only on the plant property. The odoriferous materials are usually either, cyclohexanone or unidentified organic acid combustion products.

Odor sources mentioned by two operators (9-2 and 9-3) are the organic acid incinerator flue gases and the dehydrogenation unit vent. Additionally operator 9-2 reported that the odor of cyclohexanone, from the oxidizer air vent, is detectable on plant.

F. Fugitive Emissions

Only one operator (EPA Code No. 9-1) has made an estimate of fugitive emissions - 10 SCF hr., which, if correct, is negligible. If this process becomes one for in-depth study, further study of this point will be required. For example, another estimate of fugitive emissions may be derived from information provided by operators 9-4 and 9-2. One could infer that the losses operator 9-4 assigned to his steam ejector operation (see Section III-A-2) might also include fugitive emissions. Operator 9-2, whose reported ejector losses are based - at least in part - on plant measurement, estimates only 1/30th the losses from this source that operator 9-4 estimates. If 9-2's figures are accepted then one could conclude that most of operator 9-4's estimated ejector losses are actually fugitive emissions.

IV. Emission Control

The various emission control devices that have been reported as being employed by operators of cyclohexanone/cyclohexanol plants are summarized in Table IV of this report, which is entitled Catalog of Emission Control Devices. The control devices may be divided into two broad categories; (1) Combustion Devices - those devices which depend on thermal or catalytic oxidation of combustibles for emission control, and (2) Non-combustion Devices - devices that do not depend on combustion for emission control. In Table IV, all combustion devices will be assigned two efficiency ratings (when data are available), they are:

(1) CCR - Completeness of Combustion Rating.

$$\text{CCR} = \frac{\text{Lbs. of } O_2 \text{ that react with pollutants in feed to device}}{\text{Lbs. of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

(2) SERR - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\text{weighted pollutants in} - \text{weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Most non-combustion devices will be assigned an efficiency based on percent reduction of a specific compound, with that compound defined. A few non-combustion devices will receive SERR ratings,which rating will be so designated.

Unfortunately, in only a few instances did the respondents to the cyclohexanone questionnaire provide sufficient data with which to calculate device efficiencies. Never-the-less, certain generalizations about the performance of the devices utilized can be made:

Absorber/Scrubbers

Five of the seven absorber/scrubbers reported were employed in recovering hydrocarbons from the oxidizer air vent. It is questionable whether two of these devices, CO-1A and CO-1B, should be categorized as pollution control devices. Although they prevent large amounts of hydrocarbons from entering the atmosphere, it would seem more appropriate to characterize them as product recovery devices. It seems apparent (from the general plant-to-plant agreement on total emissions) that other plants utilize such devices, but none other have included them in their listings of pollution control devices.

In general it would be expected that absorber/scrubbers would perform quite efficiently in removing hydrocarbons; which constitute over 98% of cyclohexanone/cyclohexanol's SEI. Efficiencies should be 90 + %. On the other hand, the types of absorber/scrubbers reported, would be quite inefficient in controlling emissions of carbon monoxide. Other information on these devices is tabulated in Table IV.

Condensers and K. O. Drums

Operator EPA Code No. 9-2 uses an ammonia chiller to recover cyclohexanone from his dehydrogenation unit vent. It is 98.5% effective.

However, since this $12,000 device recovers $460,000 worth of cyclohexanone per year it seems inappropriate to categorize it - primarily - as a pollution control device. Reported information on the two devices in this grouping is tabulated in Table IV.

Incineration Devices

Data sufficient to calculate device efficiencies have not been reported. However, the lack of sulfur, nitrogen or halogen containing compounds in the process would lead one to expect CCR's and SERR's of close to 100%. Operator 9-2, states that odors associated with incineration device CO-3 are a result of the incomplete combustion of organic acids, however, considering the small amount of organic material necessary to generate an odor, this does not preclude incineration efficiencies in excess of 99%. Additional information on incinerators and flares is tabulated in Table IV.

It is unlikely that any change in operating conditions can be made that will reduce air emissions since yield and selectivity are not directly related to the primary source of air pollution. For the same reason, the use of purer raw materials would have entirely negligible effect on over-all air pollution.

Development work directed toward reductions in emissions from this process falls into the following general categories - with the first preeminent:

(1) Substitution of oxygen for air; as the oxidizing agent.

(2) Substitution of another, non-pollution, oxidant for air (besides oxygen).

(3) Prevention of hydrocarbon venting to atmosphere rather than to flare.

(4) More efficient design and utilization of devices currently being utilized.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. The predicted growth rate of cyclohexanone/cyclohexanol production is 'significant' but the absolute growth to 1980 is only moderate. Furthermore, the emission data indicate that the quantity of pollutants released as air emissions is less for the subject process than for other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

Published support for the Table V forecast of new plants has not been found. The forecast is based on two assumptions:

(1) The ratio of cyclohexanone/cyclohexanol capacity to nylon 6 plus nylon 6,6 capacity does not change from year-to-year.

(2) All future cyclohexanone/cyclohexanol processes will be based on the air oxidation of cyclohexane.

A forecast based on these assumptions is most probably somewhat high, however, not to the extend that it would significantly alter the S.E.I.

On a weighted emission basis a Significant Emission Index of 6,261 has been calculated in Table VII. This is less than the S.E.I.'s calculated for some of the other processes in the study. However, it may be sufficiently high to justify an in-depth study if taken in conjunction with the processes such as adipic acid and nylon which are usually associated with cyclohexanone. Hence, it is probably expedient to defer a decision on the in-depth study of this process.

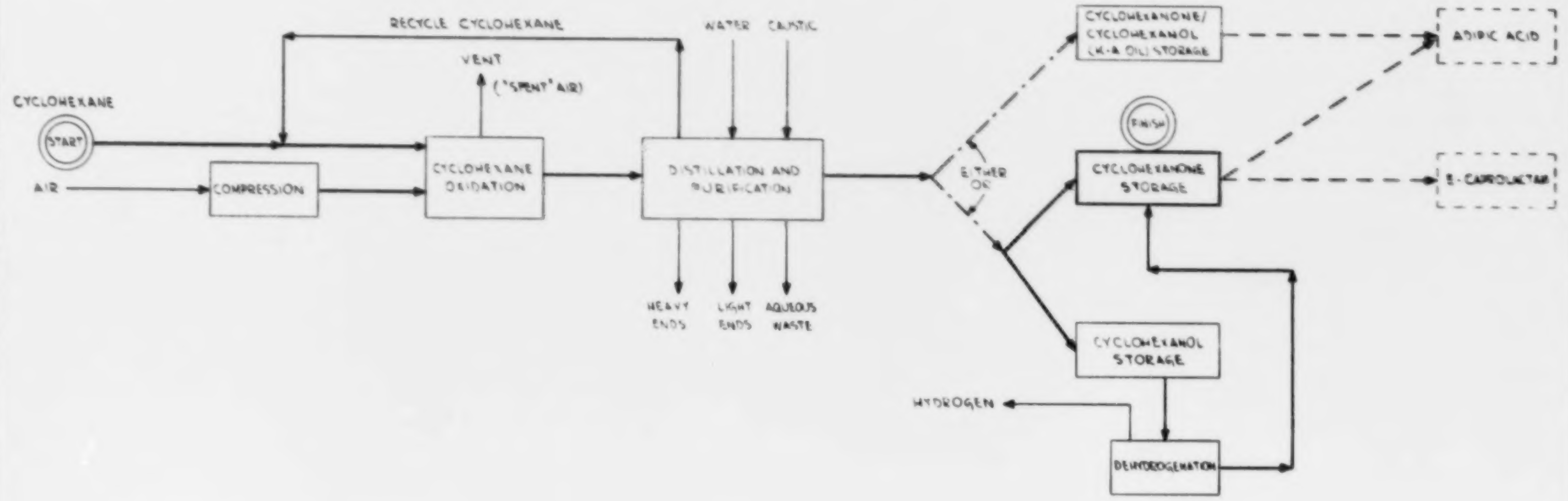
VI. Cyclohexanone/Cyclohexanol Producers

Because much of the cyclohexanone/cyclohexanol produced exists only as an intermediate rather than a final product, it is difficult to obtain dependable data concerning production capacities. Listed below are published estimates of plant capacities, for the cyclohexane air oxidation process, for the year 1967. Also a partial up-date, based on questionnaire information, is shown under the column entitled 1972 Capacity. Finally, an estimate of total 1972 capacity has been made based on the assumption that the relationship shown below is true. (at least for the time period 1967 to 1972)

$$\frac{(\text{Cyclohexanone} + \text{Cyclohexanol})\ \text{capacity}}{(\text{Nylon 6} + \text{Nylon 6,6})\ \text{capacity}} = \text{constant}_{(\text{time})}$$

Thus, 1972 capacity is estimated at 1.8×10^9 lb./yr.

Company	Location	1967 Capacity (MM Lb./Yr.)	1972 Capacity MM Lb./Yr.
Celanese	Bay City, Texas	30	24
Columbia Nipro	August, Ga.	45	150
Dow Badische	Freeport, Texas	90	252
Du Pont	Belle, W. Va.	200	Shut Down
	Orange, Texas	200	230
	Victoria, Texas	35	?
El Paso Products	Odessa, Texas	35	62
Monsanto	Pensacola, Fla.	300	414
Rohm & Hass	Louisville, Ky.	20	?
Union Carbide	Taft, La.	50	?
	Total	1005	1,800 (Est.)


CYCLOHEXANE
START
AIR
COMPRESSION
RECYCLE CYCLOHEXANE
VENT
('SPENT' AIR)
CYCLOHEXANE OXIDATION
WATER
CAUSTIC
DISTILLATION AND PURIFICATION
HEAVY ENDS
LIGHT ENDS
AQUEOUS WASTE
EITHER OR
CYCLOHEXANONE/ CYCLOHEXANOL (K-A OIL) STORAGE
FINISH
CYCLOHEXANONE STORAGE
CYCLOHEXANOL STORAGE
HYDROGEN
DEHYDROGENATION
ADIPIC ACID
E-CAPROLACTAM

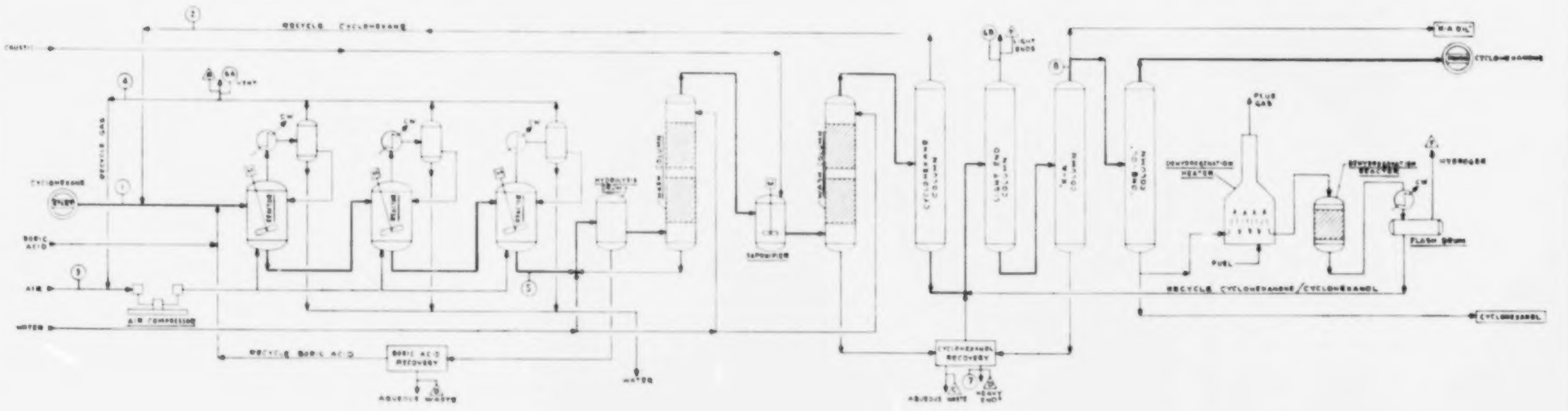
FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. 19102

FIGURE CO-1
BLOCK DIAGRAM
CYCLOHEXANONE PRODUCTION VIA AIR OXIDATION OF CYCLOHEXANE WITH ALTERNATE PRODUCTION OF "K-A" OIL

SCALE	NONE	DATE
DRAWN BY	HMP	11-16-72
CHECKED BY	RBM	12-18-72
CATALYTIC APPROVAL		
CLIENT APPROVAL	JWP	1-9-73

PROJECT NO. 42030
I.S. NO. 416
DWG. NO. R-207
REV. NO. A


CAUSTIC
RECYCLE CYCLOHEXANE
RECYCLE GAS
VENT
CYCLOHEXANE
BORIC ACID
AIR
WATER
AIR COMPRESSOR
CW
REACTOR
RECYCLE BORIC ACID
BORIC ACID RECOVERY
AQUEOUS WASTE
HYDROLYSIS DRUM
WATER
WASH COLUMN
SAPONIFIER
CYCLOHEXANE COLUMN
LIGHT END COLUMN
LIGHT ENDS
"X-A" COLUMN
"ONE-OL" COLUMN
CYCLOHEXANOL RECOVERY
AQUEOUS WASTE
HEAVY ENDS
"X-A OIL"
CYCLOHEXANONE
DEHYDROGENATION HEATER
FLUE GAS
FUEL
DEHYDROGENATION REACTOR
HYDROGEN
FLASH DRUM
RECYCLE CYCLOHEXANONE/CYCLOHEXANOL
CYCLOHEXANOL
1
2
3
4
5
6
7
8

NOTES

1. NUMBERED STREAMS - I.E. ① - IDENTIFY MATERIAL BALANCE ENTRIES (TABLE III)
2. LETTERED STREAMS - I.E. △ - IDENTIFY EMISSION CONTROL DEVICE LOCATION (TABLE IV)
3. THE PRESENTED FLOW DIAGRAM DEPICTS ONE OF THE MANY POSSIBLE CONFIGURATIONS AVAILABLE TO THE PRODUCER. [illegible] BORIC ACID VARIATION (FIG III) IS LICENSED BY [illegible] AND SD; HOWEVER THE PURIFICATION SECTION SHOWN IS NOT NECESSARILY TYPICAL OF EITHER LICENSOR'S PROCESS

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68 02 0259

PREPARED BY

FIGURE 20 V
SIMPLIFIED FLOW DIAGRAM (NOTE 3)

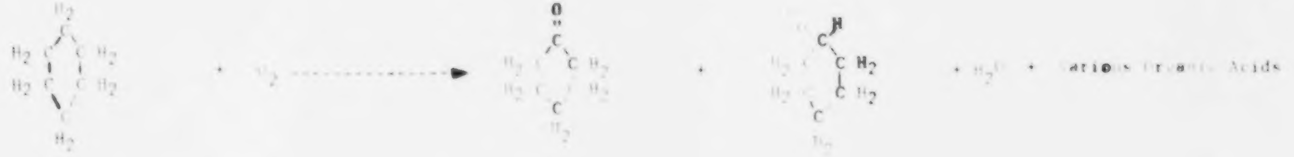
NONE
E.C.A
R-208
A

TABLE CH-I
BASIC CHEMISTRY
OF
CYCLOHEXANONE PRODUCTION

Main Reaction

Oxidation of Cyclohexane

Reaction I



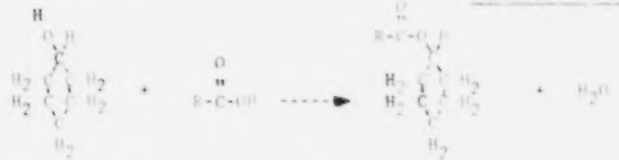
Cyclohexane + Air ----► Cyclohexanone + Cyclohexanol + Water + Acid

Mol. Wt. 84.16 98.14 100.16

Secondary Reactions

Formation of Cyclohexanol Esters

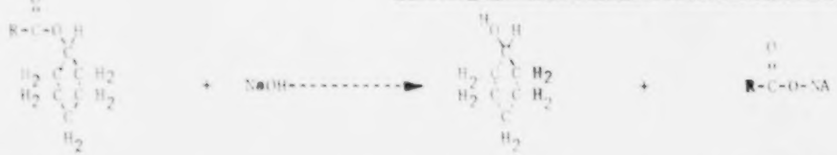
Reaction II



Cyclohexanol + Organic Acid ---► Ester + Water

Recovery of Cyclohexanol Esters (Saponification)

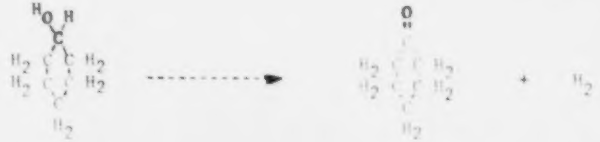
Reaction III



Cyclohexanol Ester + Caustic ---► Cyclohexanol + Sodium Salt

Cyclohexanol Dehydrogenation

Reaction IV



Cyclohexanol ---► Cyclohexanone + Hydrogen

TABLE CO-11
CYCLOHEXANE OXIDATION
TO
CYCLOHEXANONE/CYCLOHEXANOL
MATERIAL BALANCE - T/T OF "K-A OIL" PRODUCT

Stream No. (Fig. II)	1	2	3	4			5	6A & 6B	7	8
Stream Name	Fresh Feed	Recycle Liquid	Make-up Gas	Recycle Gas	Total Fd. to Rx's	Rx "Effluent" (Btms. & Ovhd.)	Rx Btms	Vent Gas	Heavy Ends	K-A Oil
Cyclohexane	0.9863	6.6600			7.6463	6.6600	6.6600			
Cyclohexanone						.1032	.1032			.1032
Cyclohexanol						.8968	.8968			.8968
Heavy Organics						.1608	.1608		.1608	
C_4 - C_5				0.0187	.0187	.0331		.0144		
O_2			.2257	0	.2257					
N_2			.7430	.9831	1.7261	1.7261		.7340		
CO				.0363	.0363	.0638		.0275		
CO_2				.0120	.0120	.0213		.0093		
Total	0.9863	6.6600	.9687	1.0501	9.6651	9.6651	7.8208	0.7942	.1608	1.0000

TABLE CO-II-A
CYCLOHEXANONE/CYCLOHEXANOL PRODUCTION
VIA
AIR OXIDATION OF CYCLOHEXANE

GROSS HEAT BALANCE

The exothermic heat of reaction is 1200 - 1300 BTU/Lb. of converted cyclohexane. (1)

There are not sufficient published data available to permit the construction of a typical commercial reactor section gross heat balance for this process.

---

(1) Mod. Text. Mag., November, 1963

TABLE CO-III
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Page 1 of 6

Plant - EPA Code Number	5-2		5-3	
Capacity - Tons of Cyclohexanone/Yr.	207,000 (5)		115,000 (8)	
Average Production - Tons of Cyclohexanone/Yr.				
Quarterly Production Variation - % of Max.	0			
Emissions to Atmosphere				
Stream	Low Pressure Off-gas (Cyclohexane Recovery Section)	High Pressure Off-gas Cyclohexane Recovery Section	Oxidizer "Spent Air" & Vent	Purification Section Vent
Flow - lb./hr.	1409	44,115	50,000	3000
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
If Intermittent - hrs./yr. flow				
Composition - Tons/ton of Cyclohexanone				
Cyclohexane				
Cyclohexanone				
Cyclohexanol				
Methane				
Ethane				
Ethylene				
Nitrogen	.01426	.80195	1.56815	.09474
Oxygen	.00016	.00470		
Hydrogen				
Carbon Monoxide	.00556	.00370	.07527	.00110
Carbon Dioxide	.00098	.00193		
Water		.00740		
Misc. Hydrocarbons			.02927	.00452
Sample Tap Location				
Date or Frequency of Sampling	Every 2 - 3 years	Bi-weekly	Infrequent	Infrequent
Type of Analysis	GLC & Orsat	GLC & Orsat	GLC	GLC
Odor Problems	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow - SCFM/Stack	250	10,000	~10,000	~600
Number	1	1	1	1
Height - Feet	65	85	160	160
Diameter - Inches	6	6	10	24 (?)
Exit Gas Temp - F°	85	85	104	104
Emission Control Devices	No	(?)	Yes	Yes
Type - Incinerator				
Flare				
Scrubber			+	+
Other				
Catalog I.D. Number			CO-11	CO-12
Total Hydrocarbon Emissions - Ton/ton of Cyclohexanone			.03379	
Total Particulate & Aerosol " " " "				
Total NO_x " " " "				
Total SO_x " " " "				
Total CO " " " "	.00926		.07637	

TABLE CO-III
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Plant - EPA Code Number	5-4		
Capacity - Tons of Cyclohexanone/Yr.	31,000 (5)		
Average Production - Tons of Cyclohexanone/Yr.			
Quarterly Production Varaition - % of Max.	0		
Emissions to Atmosphere			
Stream	Oxidizer "Spent Air" Vent		Desorbed Gases from Storage & Purification
Flow - lb./hr.	12,958		~500 (6)
Flow Characteristic - Continuous or Intermittent	Continuous		Continuous
if Intermittent - hrs./yr. flow			
Composition - Tons/ton of Cyclohexanone			
Cyclohexane	.02355		
Cyclohexanone			
Cyclohexanol			
Methane			
Ethane			
Ethylene			
Nitrogen	1.52394		
Oxygen	.02613		
Hydrogen			
Carbon Monoxide	.05560		
Carbon Dioxide	.02574		?
Water			+
Mics. Hydrocarbons	.01274		+
Sample Tap Location	Stack		
Date or Frequenyc of Sampling	Infrequently		
Type of Analysis	GLC		
Odor Problems			
Vent Stacks	Yes		Yes
Flow - SCFM/Stack	2870		
Number	1		
Height - Feet	19		
Diameter - Inches	8		
Exit Gas Temp. - F^{o}			
Emission Control Devices	No		Yes
Type - Incinerator			
Flare			
Scrubber			
Other			
Catalog I.D. Number			+ K. O. Drum CO-10
Total Hydrocarbon Emissions - Ton/ton of Cyclohexanone		~.03629	
Total Particulate & Aerosol - " " " "			
Total NO$_x$ " " " "			
Total SO$_x$ " " " "			
Total CO " " " "		~.02574	

TABLE CO-III
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Page 3 of 6

Plant - EPA Code Number		9-3				9-1
Capacity - Tons of Cyclohexanone/Yr.		51,000				12,000
Average Production - Tons of Cyclohexanone/Yr.						
Quarterly Production Variation - % of Max.		0				0
Emissions to Atmosphere	(4)	(4)				
Stream	Oxidizer "Spent Air" Vent	Oxidizer "Spent Air" Vent	Distill./Purf Waste Stream Incinerator Flue Gas	Ground Flare Flue Gas	Cyclohexanol Dehydrogenation Vent	Not Specified
Flow - lb./hr.	31,560	12,400	Not Specified	1750 Max.		
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent	Continuous	
if Intermittent - hrs./yr. flow						
Composition - Tons/ton of Cyclohexanone						
Cyclohexane	.01913	.04208				
Cyclohexanone	.00112	.00492			.00071	
Cyclohexanol	.00029	.00043			00081	
Methane					<.00001	
Ethane					<.00001	
Ethylene					.00002	
Nitrogen	+	+				
Oxygen	?	?				
Hydrogen					.02277	
Carbon Monxide	.01527	.01562				
Carbon Dioxide	?	?	+	+		
Water			+	+		
Misc. Hydrocarbons						
Sample Tap Location			Burner Stack			
Date or Frequency of Sampling	Irregular	Irregular		Never	Irregular	
Type of Analysis	GLC	GLC			GLC	
Odor Problems			Yes		No	
Vent Stacks	Not Specified	Not Specified	Yes	Not Specified	Yes	
Flow - SCFM/Stack			6814		846	
Number			1		1	
Height - Feet			36		12	
Diameter - Inches			72		8	
Exit Gas Temp. - F°			1800		70°	
Emission Control Devices	Yes	Yes	Yes	Yes	Yes	
Type - Incinerator			+			
Flare				+		
Scrubber	+	+			+	
Other						
Catalog I.D. Number	CO-5 A&B	CO-6 A&B	CO-7	CO-8	CO-9	
Total Hydrocarbon Emissions - Ton/ton of Cyclohexanone			.06968			
Total Particulate & Aerosol Emissions - Ton/ton of Cyclohexanone						
Total NO_x " " " " "						
Total SO_x " " " " "						
Total Co " " " " "			.03089			

TABLE CO-III
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Plant - EPA Code Number		9-2			
Capacity - Tons of Cyclohexanone/Yr.		75,000			
Average Production - Tons of Cyclohexanone/Yr.					
Quarterly Production Variation - % of Max		0			
Emissions to Atmosphere					
Stream	Unspecified Oxidation Section Vent	Oxidation "Air" Vent	Purification Section Steam Jet Discharge	Cyclohexanol Dehydrogenation Vent	Flue Gas ex Incineration of Various Waste Streams
Flow - lb./hr.	Not Specified	26,675	69	200	~1000 (1)
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent hrs./yr. flow					
Composition - Tons/ton of Cyclohexanone					
Cyclohexane	.00116	.00652	.00051		
Cyclohexanone		.00253		.00067	
Cyclohexanol				< .00001	
Methane				< .00001	
Ethane				< .00001	
Ethylene				.00002	
Nitrogen		1.42762	+		
Oxygen			+		+
Hydrogen				.01088	
Carbon Monoxide		.01445		.00014	+
Carbon Dioxide					+
Water					
Misc. Hydrocarbons					+
Sample Tap Location	None		None		None
Date or Frequency of Sampling	Never	1970	Never	1969	Never
Type of Analysis	Calc'd	Mass Spec & GLC	Estimate	Mass Spec & GLC	
Odor Problems	No	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes	Yes
Flow SCFM/Stack	10	6000	5	630	~15,000
Number	1	1	3	1	1
Height - Feet	40	~15	55	40	30
Diameter - Inches	1.5	16	1.5	3	72
Exit Gas Temp. F°	85°	70°	150	54	1750
Emission Control Devices	None	Yes	No	Yes	Yes
Type - Incinerator					+
Flare					
Scrubber		+			
Other				Condenser	
Catalog I.D. Number		CO-1A&B		CO-2	CO-3
Total Hydrocarbon Emissions - Ton/ton of cyclohexanone			.01141		
Total Particulate & Aerosol - " " " "					
Total NO_x " " " "					
Total SO_x " " " "					
Total CO Emissions - Ton/ton of Cyclohexanone			.01459		

TABLE CO-III
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Plant - EPA Code Number	9-4			
Capacity - Tons of Cyclohexanone/Yr	75,000			
Average Production - Tons of Cyclohexanone/Yr.				
Quarterly Production Variation - % of Max				
Emissions to Atmosphere				
Stream	Oxidation "Air" Vent			Purification Section Stream Jet Discharge
Flow - lb./hr.	38,837			Not Specified
Flow Characteristic - Continuous or Intermittent	Continuous			
if Intermittent hrs./yr. flow				
Composition - Tons/ton of Cyclohexanone				
Cyclohexane	.00383			
Cyclohexanone				
Cyclohexanol				
Methane				
Ethane				
Ethylene				
Nitrogen	1.88830			
Oxygen	.00649			
Hydrogen				
Carbon Monoxide	.10106			
Carbon Dioxide	.04069			
Water				
Misc. Hydrocarbons	.02543			.01500
Sample Tap Location				
Date or Frequency of Sampling				None
Type of Analysis	Calc'd.			Estimate
Odor Problems	No			
Vent Stacks	Yes - 2			None
Flow SCFM/Stack	3750	4580		
Number	1@	1@		
Height - Feet	60	195		
Diameter - Inches	6"			
Exit Gas Temp. F°	70°			
Emission Control Devices	No	Yes (2)		None
Type - Incinerator				
Flare		+ (2)		
Scrubber				
Other				
Catalog I.D. Number		CO-4		
Total Hydrocarbon Emissions - Ton/ton of cyclohexanone			.04426	
Total Particulate & Aerosol - " " " "				
Total NO_x " " " "				
Total SO_x " " " "				
Total CO " " " "			.10106	

TABLE CO-III
EXPLANATION OF NOTES
NATIONAL EMISSIONS INVENTORY
CYCLOHEXANONE PRODUCTION

Page 6 of 6

(1) Prior to combustion.

(2) A portion of this stream vents through an unlit flare.

(3) No entry.

(4) The quantities listed below are believed to be the sum of the emissions from the two identical streams that make up this entry.

(5) Capacity calculated by Houdry based on stated cyclohexane feed. Basis - .7673 ton cyclohexanone per ton of cyclohexane feed; ratio from questionnaire data.

(6) Flow prior to combustion in off-site flare.

(7) Operator states flow is from scrubber but gives no details.

(8) Capacity calculated by Houdry, based on pro-ration from EPA Code No. 5-2.

TABLE CO-IV
CATALOG OF EMISSION CONTROL DEVICES
CYCLOHEXANONE PRODUCTION

Page 1 of 4

	Distillation Section		Dehydrogenation Section
Absorbers/Scrubbers			
EPA Code No. for Plant Using	5-3		9-3
Flow Diagram (Fig. II) Stream I.D.	/E\ + Others		/F\
Device I.D. No.	CO-12		CO-9
Purpose - Control Emission of	C_1 to C_6 HC		Unspecified HC's
Scrubbing/Absorbing Liquid	Lean Oil		Water
Type - Spray			
Packed Column			+
Trays - Type			
Number			
Plenum Chamber			
Other			
Scrubbing/Absorbing Liquid Rate - GPM			3
Design Temp. (Operating Temp.) F°	(104)		(50)
Gas Rate - SCFM (lb./hr.)			846
T-T Height - Ft.			12
Diameter - Ft.			.67
Washing Gases to Stack	Yes		Yes
Stack Height - Ft.	160		12
Stack Diameter - Ft.	2		.67
Installed Cost - Mat'l. & Labor - $	21,000 (4)		1,000
Installed Cost Based on - "year" - Dollars	1966		1972
Installed Cost - Mat'l. & Labor ¢/lb. of Cyclohexanone/Yr.	.0913 (4)		.0010
Operating Cost - Annual $ (1972)			1200
Value of Recovered Product - $/Yr.			100
Net Operating Cost - Annual $			1100
Net Operating Cost - ¢/lb. of Cyclohexanone			.0011
Efficiency - %	84.7 (H.C.'s)		
SERR - %	84.5		
Incineration Devices			
EPA Code No. for Plant Using	9-4	9-3	9-2
Flow Diagram (Fig. II) Stream I.D.		D /E\	/B\ /C\ /D\ /E\
Device I.D. No.	CO-4	CO-8	CO-3
Types of Compounds Incinerated	Emerg. Relief	Lt. & Hvy. Ends	Various H.C.
Type Device - Flare	+		
Incinerator			+
Other		+ Ground Flare	
Materials Incinerated - SCFM (lb./hr.)	1000 GPM Liq., 311,000 PPH Vapor		
Auxiliary Fuel Req'd. (Excl. Pilot)		Yes	Yes
Type		Not Specified	
Rate - BTU/hr.			
Device or Stack Height - Ft.	195		30
Installed Cost - Mat'l. & Labor - $	127,377		Not Specified
Installed Cost Based on - "year" - Dollars	(5)		
Installed Cost - Mat'l. & Labor ¢/lb. Cyclohexanone/Yr.			
Operating Cost - Annual - $ (1972)	4000		
Operating Cost - ¢/lb. of Cyclohexanone			
Efficiency - %-CCR			
Efficiency - %-SERR			

TABLE CO-IV

CATALOG OF EMISSION CONTROL DEVICES
CYCLOHEXANONE PRODUCTION

	Oxidation Section						Hydrolysis and Saponification
Absorbers/Scrubbers							
EPA Code No. for Plant Using	9-2		9-2	9-3	9-3	5-3	
Flow Diagram (Fig. II) Stream I.D.	△A		△A	△A	△A	△A	
Device I.D. No.	CO-1A		CO-1B	CO-5A-B (1)	CO-6A & B (1)	CO-11	
Purpose - Control Emission of	Cyclohexane Cyclohexanone		Cyclohexane Cyclohexanone	C_6 HC's	Unspecified HC	Unspecified HC	
Scrubbing/Absorbing Liquid						Lean Oil	
Type - Spray							
Packed Column				+	+		
Trays - Type							
Number							
Plenum Chamber							
Other							
Scrubbing/Absorbing Liquid Rate -GPM					880 (lb./hr.)		
Design Temp. (Operating Temp.) F°				(100)			
Gas Rate - SCFM (lb./hr.)	5400		600	(28,000)	(510)		
T-T Height - Ft.				32.6	28		
Diameter - Ft.				2	1.3		
Washed Gases to Stack		Yes		Yes	Yes	Yes	
Stack Height - Ft.		15					
Stack Diameter - Ft.		1.3					
Installed Cost - Mat'l. & Labor - $	100,000		30,000	(2) 6200 (Total)	(2) 1550 (Total)	156,000	
Installed Cost Based on - "year" - Dollars	1968		1968	1962	1962	(3) 1966 & 1971	
Installed Cost - Mat'l. & Labor, ¢/lb. of Cyclohexanone/Yr.	.0667		.0200	(2) .0061 (Total)	(2) .0015 (Total)	.0678	
Operating Cost - Annual $ (1972)	16,200		2,600	(2) 6,300 (Total)	(2) 6,300 (Total)	26,700	
Value of Recovered Product - $/Yr.	60,000		60,000	0	0	0	
Net Operating Cost - Annual - $	- 43,800		- 57,400	(2) 6,300 (Total)	(2) 6,300 (Total)	26,700	
Net Operating Cost - ¢/lb. of Cyclohexanone	- .0292		- .0383	(2) .0062 (Total)	(2) .0062 (Total)	.0116	
Efficiency - %	77.5		92.9				
SERR - %		90.5					
Incineration Devices							
EPA Code No. for Plant Using							9-3
Flow Diagram (Fig. II) Stream I.D.							B & C
Device I.D. No.							CO-7
Types of Compounds Incinerated							Organic Waste
Type of Device - Flare							
Incinerator							+
Other							
Materials Incinerated - SCFM (lb./hr.)							(15,300) Max.
Auxilliary Fuel Req'd. (Excl. Pilot)							Yes
Type							Nat. Gas
Rate - BTU/Hr.							~2.7
Device or Stack Height - Ft.							36
Installed Cost - Mat'l. & Labor - $							30,600
Installed Cost Based on - "year" - Dollars							1966
Installed Cost - Mat'l. & Labor - ¢/lb. Cyclohexanone/Yr.							.0300
Operating Cost - Annual - $ (1972)							13,500
Operating Cost - ¢/lb. of Cyclohexanone							.0132
Efficiency - % - CCR							
Efficiency - %-SERR							

TABLE CO-IV
CATALOG OF EMISSION CONTROL DEVICES
CYCLOHEXANONE PRODUCTION

	Distillation Section	Dehydrogenation Section
K. O. DRUMS		
EPA Code No. for Plants Using		
Flow Diagram (Fig. II.) Stream I.D.	5-4	
Device I.D. No.	£	
Purpose - Control Emission of	CO-10	
Type - Condenser + K. O. Drum	Hydrocarbons	
Demister		
Degasser		
Other		
Design Pressure (Operating Pressure) PSIG	+ (6)	
Design Temp. (Operating Temp.) F°		
Flow Rate of Treated Stream		
Liquid - lb./hr. (GPM)		
Gas - lb./hr. (SCFM)		
T/T Height - Ft.	(119)	
Diameter - Ft.	30	
Vent Gases to Stack	6	
Stack Height - Ft.	(6)	
Stack Diam. - Ft.		
SCFM/Stack		
Installed Cost - Mat'l. & Labor - $		
Installed Cost Based on - "year" - Dollars	10,000	
Installed Cost - Mat'l. & Labor - c/lb. of Cyclohexanone/Yr.	1965	
Operating Cost - Annual - $ (1972)	0161	
Value of Recovered Product - $/Yr.	0	
Net Operating Cost - Annual $		
Net Operating Cost - c/lb. of Cyclohexanone		
Efficiency - %		
CONDENSERS		
EPA Code No. for Plant Using		
Flow Diagram (Fig. II) Stream I.D.		9-2
Device I.D. No.		£
Purpose - Control Emission of		CO-2
Primary Refrigeration Liquid		Hydrocarbons
Capacity of Refrigeration Unit - Tons		Ammonia
Gas Rate - SCFM		
Temperature to Condenser - F°		
Temperature out of Condenser - F°		
Liquid Recovered GPM		
NoneCondensibles - SCFM		
Installed Cost - Mat'l. & Labor		
Installed Cost Based on - "year" - Dollars		12,000 (7)
Installed Cost - Mat'l. & Labor - c/lb. of Cyclohexanone/Yr.		
Operating Cost - Annual - $ (1972)		.0080
Value of Recovered Products - $/Yr.		1100
Net Operating Cost - Annual - $		460,000
Net Operating Cost - c/lb. of Cyclohexanone		-458,900
Efficiency - %		
SERR - %		98.5
		98 2

TABLE CO-IV
EXPLANATION OF NOTES
CATALOG OF EMISSION CONTROL DEVICES
CYCLOHEXANONE PRODUCTION

(1) CO-'N'-A&B consists of two identical scrubbers - one threats 40% of stream (2 reactors?) and the other 60% of the stream (3 reactors?).

(2) Assumed to be total for both CO-'N'-A and CO-'N'-B, but it may be amount for each.

(3) $106,000 in 1966 and $50,000 in 1971.

(4) Excludes original cost of column - which was initially purchased for other service.

(5) $56,377 in 1965, $48,000 in 1971 and $23,000 in 1972.

(6) K. O. Drum is located up-stream of an off-site flare. Flare not described in this report.

(7) Major equiptment cost specified as $6,000, installation estimated (Houdry) as $6,000.

TABLE CO-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity On-stream in 1980	Demand 1980	Capacity 1980	Capacity to be added 1980	Economic Plant Size	Number of New Units
1800 [a]	180 [b]	1620	3600	3600 [a]	1980	200	9 - 10

Notes:

General - All rates are MM Lbs./Yr.
a - See Section VI (one-ol Producers) for source.
b - Arbitrary assumption.

TABLE CO-VI
EMISSION SOURCE SUMMARY
TON/TON OF CYCLOHEXANONE/CYCLOHEXANOL

Emissions	Source					Total
	Oxidation	Hydrolysis and Saponification	Distillation	Dehydrogenation	Fugitive Emissions	
Hydrocarbons	.037	↑	.001	.001	↑	.039
Particulates & Aerosol		Negligible			Negligible	
NO_x						
SO_x						
CO	.042	↓	.001		↓	.043

TABLE CO-VII
WEIGHTED EMISSION RATES

Chemical - Cyclohexanone/Cyclohexanol

Process - Air Oxidation of Cyclohexane

Increased Capacity by 1980 - 1980 MM Lb./Yr.

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	.039	77.2	80	6176
Particulates	0		60	
NO_x	0		40	
SO_x	0		20	
CO	.043	85.1	1	85

Significant Emission Index = 6261 (MM Lbs./Yr.)

Dimethyl Terephtalate (and TPA)

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V.	Significance of Pollution	DT-10
VI.	TPA/DMT Producers	DT-11

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Net Material Balance (Amoco Process only)	Table DT-I
Gross Heat Balance	Table DT-II
Emission Inventory	Table DT-III
Catalog of Emission Control Devices	Table DT-IV
Number of New Plants by 1980	Table DT-V
Weighted Emission Rates	Table DT-VI

I. Introduction

Dimethylterephthalate and terephthalic acid are used almost exclusively to produce polyester fibres and films. The polyester, polyethylene terephthalate, can be produced either by the transesterification of dimethylterephthalate (DMT) or by the direct esterification of terephthalic acid (TPA). Until 1963, technological limitations prevented the utilization of more desirable direct esterification route (i.e., ex TPA). Today, about 25% of polyethylene terephthalate (PET) production is based on direct esterification and by 1980 more than 50% will be.

The delay in the utilization of the TPA based process is attributable to the requirement for very high purity monomer in the production of polyethylene terephthalate. Prior to 1963, monomer produced from TPA did not meet the required standards of purity. This resulted primarily from the difficulty in purifying TPA itself, which is extremely insoluble in both water and most common organic solvents. Additionally, it does not melt (it sublimes). DMT, on the other hand, is susceptible to most common methods of purification and thus, was the source of all PET monomer at that time.

In 1963, new methods of producing and purifying TPA were commercialized. Today, both Amoco and Mobil are producing high purity TPA in the U. S. Amoco is utilizing the Mid-Century oxidation process and Mobil is using Olin-Mathieson technology. Currently, Amoco's high purity TPA capacity is about four times Mobil's, with some observers predicting continued dominance in that field until at least the end of the decade. DuPont, Hercules, Hystron and Tennessee Eastman continue to utilize DMT technology (although Hercules is thought to be constructing some capacity based on TPA).

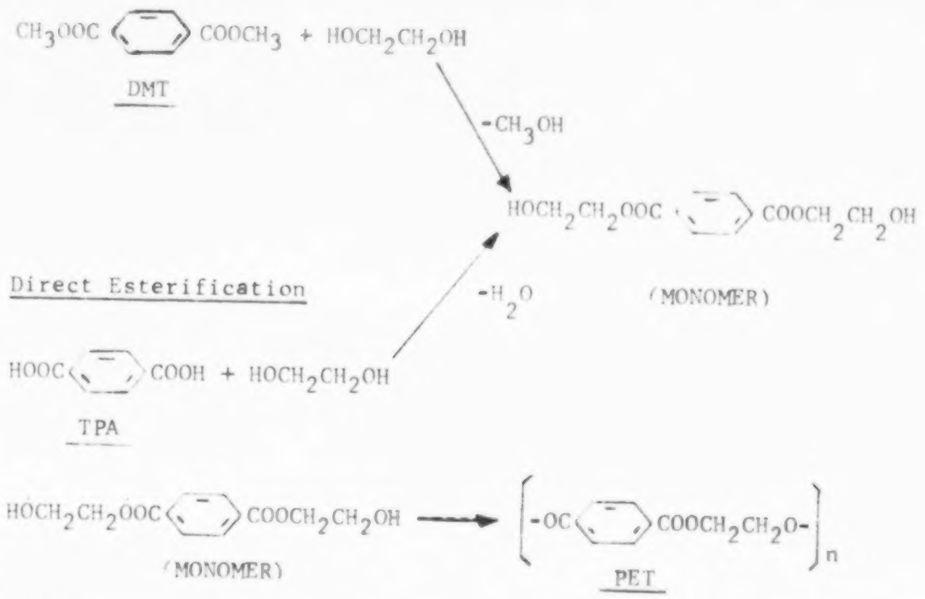
A general characterization of the atmospheric emissions resulting from the production of DMT and TPA is difficult, because of the variety of processes utilized. From process to process emissions vary considerably, both qualitatively and quantitatively. At best, one might characterize the emissions as "moderate". Fortunately, Amoco's process appears to be one of the lowest polluters and its predicted preeminence will have a suppressing influence on total future emissions.

Current TPA and DMT capacity in the U. S. is about 2.9 x 10^9 lbs./year (of equivalent DMT). If the industry grows at an annual rate of 9½%, 1980 capacity will be 5.9 x 10^9 lbs./year.

II. Process Description

There are currently five different processes utilized in the U S for the production of TPA and DMT. All production ends up as polyethylene terephthalate via transesterification or direct esterification as shown below:

Transesterification


CH_3OOC … $COOCH_3$ + $HOCH_2CH_2OH$
DMT
$-CH_3OH$
$HOCH_2CH_2OOC$ … $COOCH_2CH_2OH$
(MONOMER)
Direct Esterification
$-H_2O$
$HOOC$ … $COOH$ + $HOCH_2CH_2OH$
TPA
$HOCH_2CH_2OOC$ … $COOCH_2CH_2OH$
(MONOMER)
$-OC$ … $COOCH_2CH_2O-$
n
PET

Brief descriptions of each of the five processes follow:

Amoco Process (TPA) (Also see Flow Diagram Figure DT-1)

This process was originally developed by the Mid-Centry Corporation, now a wholly owned subsidiary of Standard Oil Company of Indiana. Previously, the Mid-Century Corporation was a joint venture between Halcon International and Standard Oil.

The method is based on the liquid phase oxidation of P-xylene with air. Oxidizer operating conditions are about 400° F and 400 PSIG. The P-xylene feed is diluted with glacial acetic acid and small amounts of manganese acetate or cobalt acetate plus a bromide are added as catalysts.

Oxidizer conditions are highly corrosive and require appropriate high alloy vessels.

The purification portion of the Amoco process involves the hydrogenation of crude TPA over a palladium containing catalyst at about 450° F. High purity TPA is recrystallized from a high pressure water solution of the hydrogenated material.

Mobil Process (TPA)

In 1963 Mobil purchased exclusive world-wide rights to Olin-Mathieson high purity TPA technology. Subsequent development work lead to the construction of Mobil's facility at Beaumont, Texas.

This process, like the Amoco process is based on the liquid phase oxidation of P-xylene in an acetic acid media. Mobil, however, utilizes 95% oxygen, rather than air as the oxidizing agent. Another characteristic of the process is the use of methyl ethyl ketone as the activator for the cobalt catalyst. Oxidation takes place at about 265° F in a battery of parallel stirred reactors.

The first stage purification involves slurrying the TPA with hot acetic acid and charging it to a soaking chamber, where impurities are leached from the crude product. This material is washed on a continuous filter and dryed with hot nitrogen. This (now) technical grade TPA is suitable for DMT manufacture, however, further purification is required to obtain TPA of high enough purity for fiber-grade polymer manufacture via direct esterification.

The final purification step consists essentially of a continuous sublimation and condensation procedure. The technical grade of TPA is combined with small quantities of hydrogen and a solid catalyst, disperesed in steam, and transported to a furnace. There the TPA is vaporized and certain of the contained impurities are catalytically destroyed. Catalyst and non-volatile impurities are removed in a series of filters, after which the pure TPA is condensed and transported to storage silos.

DuPont Process (DMT)

The Calico Printers Association in the United Kingdom developed a polymerization process based on nitric acid oxidation to produce TPA. The rights to this process were bought by DuPont in 1944. The process was also formerly used by ICI, BASF and Farbwerke Hoechst.

TPA is produced by oxidizing P-xylene with air and nitric acid. After various washing operations the TPA is dewatered and dried. DMT is formed by the direct esterification of TPA with excess methanol. The esterification takes place in a continuous stirred pressure vessel below 300° F. A small amount of sulfuric acid is used as a catalyst. After about two hours reaction time, cooling of the reactants allows the DMT to crystallize out. The DMT is separated via filtration. Impurities are removed from the DMT by melting it and distilling the molten material.

Hercules Process (DMT)

This process was originally developed by Chemische Werke Witten and engineered by Imhausen International Company. A modification of the Witten process was developed by the California Research Corporation and is used by both Hercules and Hystron. The bulk of world DMT production is based on Witten-Imhausen technology.

P-xylene is oxidized with air, under relatively mild conditions of temperature and pressure to P-toluic acid, which is then esterified to its methyl ester. The P-methyl toluate is oxidized under more severe conditions to monomethyl terephthalate. The monomethyl ester is again esterified to form DMT. Oxidation and esterification both take place in the same vessel. Chemical intermediates from the esterification step are recycled back to the oxidative portion of the process. Note that TPA is not an intermediate in this process

Tennessee Eastman Process (DMT)

Very little information is available on the Tennessee Eastman process. The TPA portion of the process is thought to be similar to the Amoco process. One source states that it involves the air oxidation of P-xylene in acetic acid solution in the presence of a cobalt catalyst. Supposedly, the use of an aldehyde promoter permits oxidation at lower temperatures and pressures than employed by Amoco. One must assume that normal esterification and DMT purification techniques would follow.

III. Plant Emissions

A. Continuous Air Emissions

1. Oxidizer Vent

This vent constitutes one of the main sources of emissions for all processes. Noxious emissions are primarily carbon monoxide and hydrocarbons, although the plant utilizing nitric acid also discharges various oxides of nitrogen. Generally speaking, there is little variation in the rate of discharge of either carbon monoxide or hydrocarbons, as reported by the various respondents. Carbon monoxide emissions vary from .02 to .03 (lbs. of pollutant per pound of product). Hydrocarbon emissions vary from .002 to .009 lbs./lb.

2. Purification Section Vents

Surprisingly, the emissions from this portion of the various processes are as significant as the emissions from the oxidizing section, despite the fact that most respondents report using air as the oxidant. Because the methods of purification run the gamut from distillation and crystallization to continuous leaching and sublimation, it is difficult to summarize or even categorize them here. The reader is referred to Table III - National Emissions Inventory, for a complete tabular summary.

3. Solvent and Methanol Recovery

Most processes utilize either methanol during the esterification step or some hydrocarbon solvent during TPA or DMT purification. Generally, facilities are provided to recover and/or repurify these relatively volatile compounds. Five sources of emissions associated with these operations are reported, all of them relatively minor with the exception of one. Respondent 10-4 reports the emission of .08 lbs. MeOH/lb. of DMT apparently as a result of operations of the type described. This seems exceptionally high, but details of the exact operation involved have not been provided.

B. Intermittent Air Emissions

1. Emergency Vents

Only two respondents, plants 10-4 and 10-7, reported emissions from this type of source. Neither made an estimate of emissions but their expected infrequency and shortness of duration should preclude the discharge of significant quantities of pollutants on a lb./lb. basis. However, instantaneous emission rates could be quite high. It seems reasonable to surmise that most of the TPA/DMT plants have some provision for emergency pressure relief.

2. Product Storage Silo Vents

Respondent 10-5 reports the intermittent emission of small quantities ($<$.00001 lbs./lb.) of fine TPA 'powder' during certain product transportation operations.

3. Incinerator Flue Gas

Respondent 10-5 utilizes a residue incinerator on an intermittent basis. According to his report, the flue gas from the incinerator contains neither unburned hydrocarbons, NO_x or SO_x. However, he does show the emission of .00012 lbs./lb. of metal oxides from this source.

C. Continuous Liquid Wastes

1. Waste Water

The following tabulation summarizes the quantity and method of treatment reported by all respondents.

Plant EPA Code No.	Quantity	Disposition
10-1	325 GPM	Treated
10-2	300 GPM	Deep Well Injection
10-4	200-250 GPM	Treated
10-5	100 GPM	Treated
10-6	787 GPM	Untreated
	26 GPM	Treated
10-7	700 GPM	Biologically Treated

2. Other Liquid Wastes

A moderate number of liquid waste streams were indicated on the flow diagrams accompanying the returned questionnaires. However, because the questionnaire was directed primarily toward eliciting information about air emissions, few details concerning these waste liquid streams were made available. Respondents did report the following:

Plant No.	Type of Liquid Waste	Quantity	Disposition
10-2	Sludge	2.3 tons/day	Retained in pits
10-5	'Liquid Waste'	6,200 tons/year	Incinerated
10-6	Sludge	1,000,000 lbs./yr.	
10-7	Distillation Heels	400 lbs./hr.	Buried
	Purification Heels	5,000 lbs./hr.	Burned in boiler house

D. Solid Wastes

Three respondents reported the generation of solid waste material. The operator of plant 10-1 reported that 350 lbs./day of solid wastes were removed from the plant site and incinerated. 525,000 lbs./year of solid wastes are incinerated by plant 10-6. The operator of plant 10-4 reports that 400 lbs./day of solid wastes are accumulated and disposed of in a sanitary land fill area.

E. Fugitive Emissions

Only the operator of plant 10-7 has offered a quantitative estimate of these emissions. He places these losses at 0.01% of flow or 25,800 lbs./year of P-xylene and 18.000 lbs./year of methanol. Perhaps the methanol losses of operator 10-4 (as described in Section III, A-3) should be included here, however, they are several orders of magnitude greater than the losses estimated by respondent 10-7.

IV. Emission Control

The emission control devices that have been reported as being employed by the operators of the various TPA/DMT plants are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\sum(\text{pollutant} \times \text{weighting factor})\text{in} - \sum(\text{pollutant} \times \text{weighting factor*})\text{out}}{\sum(\text{pollutant} \times \text{weighting factor*})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Normally, a combustion type control device (i.e., incinerator, flare, etc.) will be assigned both a "CCR" and an "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

Data sufficient to permit calculation of control device efficiency were available for only about 40% of the devices reported as being employed. A few general comments regarding their reported and expected performances seem in order:

Absorbers and Scrubbers

Nearly half of the control devices reported consisted of, at least in part, some type of absorber or scrubber. These devices are identified in Table IV as items DT-2, DT-4, DT-6 through 9, and DT-12 and DT-17. Of these, efficiencies were calculable only for DT-4, DT-6 and DT-7, where SE's of from 93.8 to 99.4 were observed. With the exception of item DT-17, the general similarity of duty and scrubber type would lead one to expect that the calculated efficiencies would be representative of the performance of all the scrubbers/absorbers listed in Table IV. Scrubber DT-17, however, is used to control the amount of TPA emitted from containers of hot sludge (via sublimation). Thus, this device must condense the sublimate and remove the condensed particles from the transporting air stream. Scrubber efficiency for this service has not been defined and would be difficult to estimate.

Bag Filters

Three bag filters are listed in Table IV, they are designated as devices DT-10, DT-13 and DT-14. (A fourth device, item DT-11, is also listed here, for convenience in cataloging.) All are used to prevent the emission to TPA 'fines' to the atmosphere. Dust collection efficiency or specific efficiency is listed as 100% for two of the devices and probably at least approaches 100% for the other. This is the type performance one would predict for bag filters in this service. Deviations from this figure would most probably result from mechanical malfunctions such as bag rupture, etc.

Incineration Devices

Three different types of incineration devices are listed in Table IV. Device DT-5 is a more-or-less standard thermal incinerator, it is reported to combust organic acids and methanol with an efficiency of 99%. Device DT-15 is a catalytic incinerator, which is reported to convert 85% of the NO_x in its feed gases to N_2. Device DT-16 is a flare used to burn dimethyl ether. Performance data are not available on this device but a CCR efficiency of 90% would be expected. Thus, all three devices are performing about as one might expect; i.e., performance is within established ranges. No reports of NO_x generation in DT-5 or DT-16 are available.

Condensers

Devices DT-1 and DT-3 are shell and tube water condensers. They are used to prevent the loss of xylene from xylene storage tank vents. Considering the relatively high boiling point of P-xylene (281° F), these simple devices should be reasonably efficient. Actual emissions would depend on tank level change rates and temperatures.

Development work aimed at reducing atmospheric emissions should be concentrated in the following areas:

(1) For processes utilizing air oxidation-substitute oxygen.

(2) For processes utilizing nitric acid as the oxidant-substitute oxygen.

(3) More efficient design and fuller utilization of control devices currently available.

V. Significance of Pollution

It is recommended that the decision, as to whether or not an in-depth study of this process should be made, be held in abeyance. The reported emission data indicate that the quantity of pollutants released as air emissions varies considerably from process to process. A weighted average of the quantity of pollutants emitted from all TPA/DMT processes (1) is less than that of some of the processes that are currently being studied. However, the SEI for this process may be based on an understated capacity growth rate (2) or on an inaccurate estimate of distribution of new capacity among the competing processes. Moderate errors in either of these assumptions would most probably result in assigning too a low a numerical value to the SEI. Also, because considerable incentive exists to develop new technology, new processes may emerge and attain significant stature in a relatively short time. The processes that might fall within this category are the Teijin Process, a nitrile process - such as the recently announced (3) Lummus Process, or the Henkel II Process.

The methods outlined in Appendix IV of this Report have been used to estimate the total weighted annual emissions from the new plants. The calculations are summarized in Tables V and VI.

Published support for the Table V forecast of 1980 capacity may be found in the O & GJ of March 17, 1972. Earlier references, such as CEH report on DMT/TPA of December, 1970, show estimates of 1980 capacity that are about 20% lower than current projections. The Table V forecast indicates economic plant size at 300 MM lbs./year capacity. The O & GJ article predicts that by 1980 the economic plant size may well be double that figure.

On a weighted emission basis, a Significant Emission Index of 6,036 has been calculated in Table VI. This is less than the SEI's of various other processes under study, however, for the reasons outlined above, it is recommended that no decision on the necessity of conducting an in-depth study of this process be made at this time.

---

(1) See Table VI footnote.

(2) Some references put DMT/TPA growth at 12%/year and high purity TPA at 23% per year, see CEN, April 2, 1973.

(3) CEN, March 19, 1973.

VI. Producers of TPA and DMT

The following tabulation shows published information regarding plant capacities and location. Various references show significant variations in their estimates of certain plant capacities.

Plant	Location	Capacity - MM Lbs./Yr. TPA	Capacity - MM Lbs./Yr. DMT
Amoco	Joliet, Ill.	150	
	Decatur, Ala.	412	
			(657)*
DuPont	Old Hickory, Tenn.		360
	Gibbstown, N. J.		300**
Hercules	Burlington, N C.		100
	Wilmington, N. C.		600
Hystron	Spartanburg, S. C.		100
Mobil	Beaumont, Texas	144	(168)*
Tennessee Eastman	Kingsport, Tenn		580
			Total = 2,865

*Equivalent DMT (= 1.17 x TPA).

**Believed to be shut down or shutting down with new capacity to be picked up at other sites.

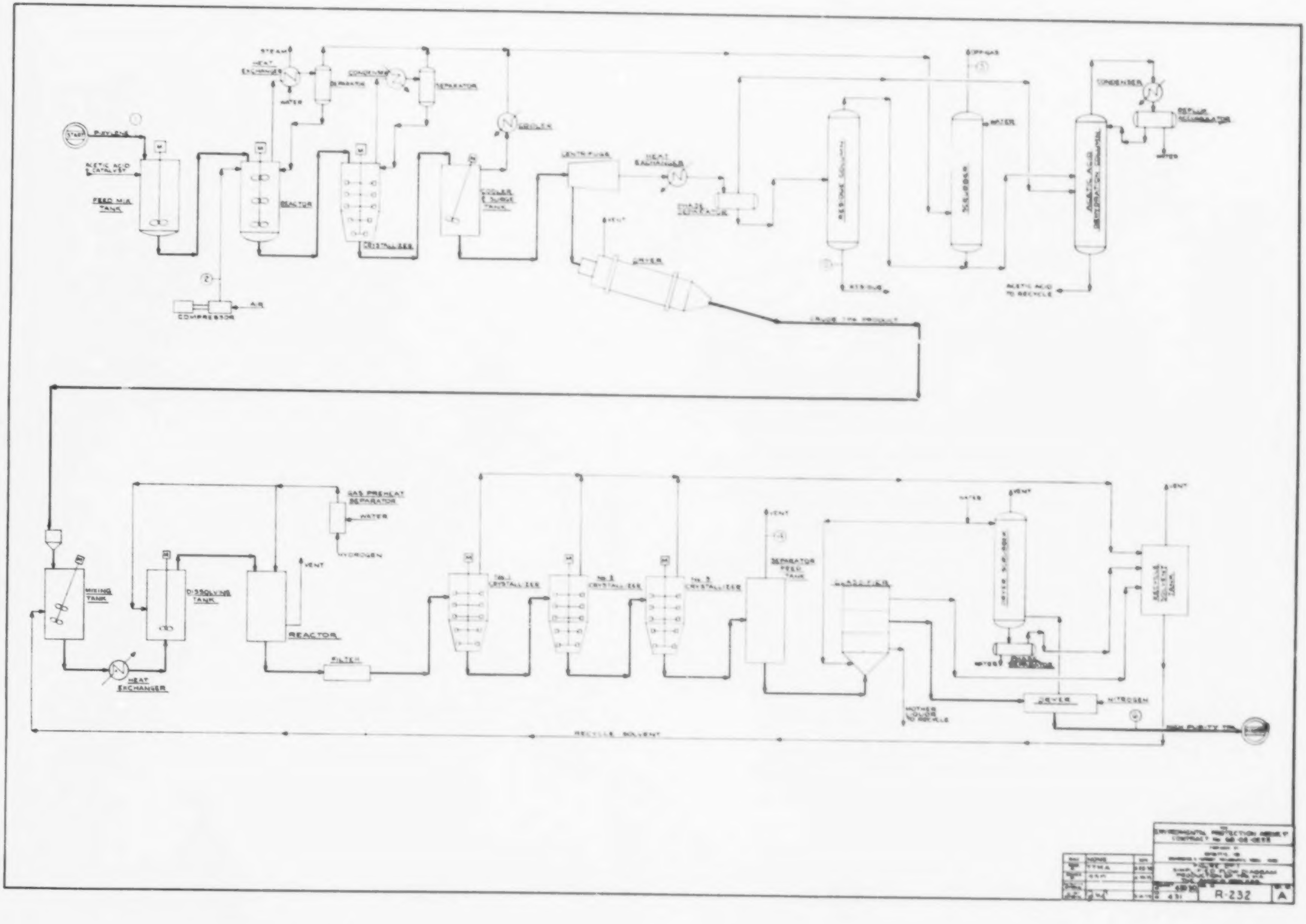

START
P-XYLENE
ACETIC ACID & CATALYST
FEED MIX TANK
REACTOR
COMPRESSOR
AIR
STEAM
HEAT EXCHANGER
WATER
SEPARATOR
CONDENSER
SEPARATOR
CRYSTALLIZER
COOLER
COOLER & SURGE TANK
CENTRIFUGE
VENT
DRYER
HEAT EXCHANGER
PHASE SEPARATOR
RESIDUE COLUMN
RESIDUE
SCRUBBER
OFFGAS
WATER
ACETIC ACID DEHYDRATION COLUMN
CONDENSER
REFLUX ACCUMULATOR
WATER
ACETIC ACID TO RECYCLE
CRUDE TPA PRODUCT
MIXING TANK
HEAT EXCHANGER
DISSOLVING TANK
REACTOR
VENT
GAS PREHEAT SEPARATOR
WATER
HYDROGEN
FILTER
No. 1 CRYSTALLIZER
No. 2 CRYSTALLIZER
No. 3 CRYSTALLIZER
VENT
SEPARATOR FEED TANK
CLASSIFIER
MOTHER LIQUOR TO RECYCLE
WATER
VENT
DRYER
NITROGEN
RECYCLE SOLVENT TANK
VENT
HIGH PURITY TPA
RECYCLE SOLVENT
ENVIRONMENTAL PROTECTION AGENCY
431
R-232
A

TABLE DT-I
TYPICAL MATERIAL BALANCE FOR TEREPHTHALIC ACID PRODUCTION BY THE AMOCO PROCESS (T/T TPA)

Stream Nos. (e)	1	2	3	4	5	6
Component	Xylene Feed	Air	Vent Gas	Distillation Reject	Purification Reject	Product
CO			.0707 (b)			
CO_2			.1128 (b)			
N_2		2.6056	2.6056			
O_2		0.7914	.0348			
P-Xyl	0.7100					
M, O-Xyl & ET Bz	0.0072					
HAC	(d)			+	+	
Heavy Ends (a)					.0050	
TPA						1.0000
Impurities				.0104		
H_2O				.2749		
	0.7172	3.3970	2.8239	.2853	.0050	1.0000

(a) Quinones and ketones.
(b) Assumes 90% of non-selectivity goes to equal volumes of CO and CO_2.
(c) Isophthalic acid, benzoic acid, O-toluic acid and acetophenone resulting from feed impurities.
(d) HAC/xylene ratio unknown, but there is large excess of HAC.
(e) Refer to stream numbers of Figure DT-I.

TABLE DT-II
TPA AND DMT
EX
P-XYLENE OXIDATION
(AMOCO PROCESS)

GROSS REACTOR HEAT BALANCE

A reasonable estimate of the oxidizer heat balance for this process is impossible because the acetic acid/P-xylene ratio is not available from the literature. It is well known that the reaction is quite exothermic.

The heat of reaction for the oxidation of P-xylene to terephthalic acid is estimated to be of the order of 3200 BTU/lb. of TPA.

TABLE DI-III
NATIONAL EMISSION INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Plant EPA Code No.	10-1 (A)		
Product	TPA		
Capacity, Tons of DMT or (Equivalent DMT)*/Yr.	(290,000)		
Emissions to Atmosphere			
Stream	Oxidizer Vent	Filter, Dryer Silo Vent	Distillation Section Vent
Flow - Lbs./Hr.	256,000	18,470	
Flow - Continuous or Intermittent	Continuous	Continuous	
if Intermittent - Hrs./Yr. Flow			
Composition - Ton/Ton DMT or (Equivalent DMT)			
TPA		(.00036)	
Acetic Acid		(.00348)	(.00028)
Water		(.00227)	
Carbon Monoxide	(.01886)	(.00131)	
Carbon Dioxide	(.11895)	(.00852)	
Oxygen	(.25946)	(.02167)	
Nitrogen	(3.44695)	(.24011)	(.00259)
Methyl Acetate	(.00308)		(.00068)
Xylene	(.00077)	(.00005)	
Propyl Acetate			(.00003)
Acetaldehyde	(.00077)		(.00066)
Dimethyl Ether			
Methyl Alcohol			
Sulfur Dioxide			
DMT			
Metal Oxides			
Benzoic Acid			
P-Toluic Acid			
P-Carboxyl Benzaldehyde			
Hydrogen			
Misc. Light Hydrocarbons - as Methane	(.00039)		
Vent Stacks		Yes	Yes
Number		18	4
Height - Feet		31 to 64	21 to 40
Diameter - Inches		3 to 10	2 to 4
Exit Gas Temp. - F°			
SCFM/Stack			
Type of Emission Control Device Employed		None	None
Control Device I. D. No.			
Analysis			
Date or Frequency of Sampling		Monthly	Monthly
Sample Tap Location		At Vent	At Vent
Type of Analysis		GLC	GLC
Odor Problem		No	No
Summary of Air Pollutants - T/T of DMT or (Equivalent)			
Hydrocarbons	(.00980)		
Particulates or Aerosols	(.00036)		
NO_x			
SO_x			
CO	(.02017)		

(A) Plants 10-1 and 10-6 are part of the same overall facility.

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Page 2 of 7

Plant EPA Code No.		10-2		
Product		TPA		
Capacity, Tons of DMT or (Equivalent)/Yr.**		(84,240)		
Emissions to Atmosphere				
Stream	Oxidizer Vent	Condensation Section	Condensation Section	Incinerator Flue Gas
Flow - Lbs./Hr.	Unknown	97,035	105,597	Unknown
Flow - Continuous or Intermittent		Continuous	Continuous	
if Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton DMT or (Equivalent DMT)				
TPA		(.00107)	(.00116)	
Acetic Acid		(.00024)	(.00026)	
Water		(4.00158)	(4.35466)	
Carbon Monoxide		(.00482)	(.00525)	
Carbon Dioxide		(.00061)	(.00066)	
Oxygen				
Nitrogen				
Methyl Acetate				
Xylene				
Propyl Acetate				
Acetaldehyde				
Dimethyl Ether				
Methyl Alcohol				
Sulfur Dioxide				
DMT				
Metal Oxides				
Benzoic Acid		(.02485)	(.02704)	
Para Toluic Acid		(.00021)	(.00023)	
Para Carboxyl Benzaldehyde		(.00003)	(.00003)	
Hydrogen		(.00146)	(.00159)	
Misc. Light Hydrocarbons - as Methane		(.01182)	(.01286)	
Vent Stacks	Yes	Yes	Yes	Yes
Number	1	1	1	1
Height - Feet	64	120	120	50
Diameter - Inches	24	72	72	52
Exit Gas Temp. - F°	212	310	310	550
Flow - SCFM/Stack		73,000		
Emission Control Device	Yes	Yes	Yes	No
Type	Scrubber	Bag Filter	Bag Filter	
I. D. Number	DT-12	DT-13	DT-14	
Analysis				
Date or Frequency of Sampling	Never	"As Required"	"As Required"	None
Sample Tap Location		@ Platform	@ Platform	
Type of Analysis		EPA Method No. 5 & Design Calc'd	EPA Method No. 5 & Design Calc'd	
Odor Problem	No	No	No	
Summary of Air Pollutants T/T of DMT or (Equivalent DMT)				
Hydrocarbons		(.07757)		
Particulates & Aerosols		(.00223)		
NO_x		0		
SO_x		0		
CO		(.01007)		

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Plant EPA Code No. 10-4
Product DMT
Capacity, Tons of DMT or (Equivalent DMT)*/Yr 300,000

Emissions to Atmosphere Stream	Oxidizer Vent	Incinerator Flue Gas	Purification Section Scrubber Vent	Purification Emergency Vent	Reactor Section Ejector Discharge	Purification Vent	Other Emissions
Flow - Lbs./Hr.	229,000	69,850	5,034	Unknown	942	8	5,720
Flow - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent	Continuous	Continuous	Unknown
If Intermittent - Hrs./Yr. Flow				15 Sec./Incident			
Composition - Ton/Ton DMT or (Equivalent DMT)							
TPA							
Acetic Acid							
Water	.01395	.29230	.00022		.00031	.00001	
Carbon Monoxide	.03096	.00223	.00068	+	.00002		
Carbon Dioxide	)	)	)	+	)	)	
Oxygen	)3.14856	).67985	).06919	+	).01209	).00006	
Nitrogen	)	)	)		)	)	
Methyl Acetate							
Xylene	.00938		TR		.00075	.00003	
Propyl Acetate							
Acetaldehyde							
Dimethyl Ether							
Methyl Alcohol			.00031	+			.0800
Sulfur Dioxide		.00255					
DMT				+			
Metal Oxides							
Benzoic Acid							
P-Toluic Acid							
P-Carboxyl Benzaldehyde							
Hydrogen							
Misc. Light Hydrocarbons - as Methane							
Vent Stacks	Yes	Yes	Yes	Not Specified	Yes	Not Specified	No
Number	2?	1	1		2?		
Height - Feet	100	100	90		60		
Diameter - Inches	30	60	12		6		
Exit Gas Temp. - F°	85	450	50		85		
SCFM/Stack	25,000	1,800	600		100		
Type of Emission Control Device Employed	Absorber	Incinerator	Scrubber	None	Scrubber	None	None
Control Device I. D. No.	DT-4	DT-5	DT-6		DT-7		
Analysis				None	None	None	None
Date or Frequency of Sampling	Weekly	Weekly	Semi-Weekly				
Sample Tap Location	Stack Base	@ WHB	Scrubber Outlet		At Scrubber		
Type of Analysis	GLC	Various	GLC & Gas Partitioner		Calc'd	Calc'd	Calc'd.
Odor Problem	No	No	No	No	No	No	
Summary of Air Pollutants - T/T of DMT or (Equivalent)							
Hydrocarbons			.09047				
Particulates or Aerosols			+				
NO_x							
SO_x			.00255				
CO			.03389				

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Page 4 of 7

Plant EPA Code No.	10-5				
Product	TPA				
Capacity, Tons of DMT or (Equivalent)/Yr.	(241,000)				
Emissions to Atmosphere					
Stream	Oxidizer Vent	Surge Tank Vent	Storage Silo Vent	Residue Incinerator Flue Gas	Solvent Dehydrator
Flow - Lbs./Hr.	5,720	1,238	11,428	74,508	15,650
Flow - Continuous or Intermittent	Continuous	Continuous	Intermittent	Intermittent	Continuous
If Intermittent - Hrs./Yr. Flow			82	7,344	
Composition - Ton/Ton DMT or (Equivalent DMT)					
TPA			(< .00001)		
Acetic Acid	(.00163)	(.00024)			(.00025)
Water	+	(.00229)		)	(.26357)
Carbon Monoxide	(.01591)		(< .00001)	)	
Carbon Dioxide	)	)	)	)(1.13502)	
Oxygen	)(2.43726)	)(.01823)	)(.19346)	)	
Nitrogen	)	)	)	)	
Methyl Acetate	(.00513)	(.00020)			(.00110)
Xylene					
Propyl Acetate					
Acetaldehyde					
Dimethyl Ether					
Methyl Alcohol					
Sulfur Dioxide					
DMT					
Metal Oxides				(.00012)	
Benzoic Acid					
Para Toluic Acid					
Para Carboxyl Benzaldehyde					
Hydrogen					
Misc. Light Hydrocarbons - as Methane					
Vent Stacks	Yes	Yes	Yes	Yes	No
Number	1	1	1	1	
Height - Feet	77	65	140	125	
Diameter - Inches	18	18	12	42	
Exit Gas Temp. - F°	116	120	275	600	
Flow - SCFM/Stack	32,150	300	2,000	16,550	
Emission Control Device	Yes	Yes	Yes	Yes	No
Type	High Pressure Absorber	Scrubber	Bag Filter	Precipitator	
I. D. Number	DT-8	DT-9	DT-10	DT-11	
Analysis					
Date or Frequency of Sampling	Occasional	Occasional	Never	Never	Once/Shift
Sample Tap Location	Accessible	Accessible	Accessible		Accessible
Type of Analysis	GLC	GLC	Calc'd	Calc'd	Titration
Odor Problem	No	No	No	No	No
Summary of Air Pollutants T/T of DMT or (Equivalent DMT)					
Hydrocarbons			(.00855)		
Particulates & Aerosols			(.00012)		
NO_x			0		
SO_x			0		
CO			(.01591)		

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Plant EPA Code No.	10-6 (A)				
Product	DMT				
Capacity, Tons of DMT or (Equivalent DMT)*/Yr.	290,000				
Emissions to Atmosphere					
Stream	Reactor Vent	Methanol Recovery Vent (B)	Methanol Recovery Vent		Crude Product "Hold-Up" Vent
Flow - Lbs./Hr.	2	~2	415		3
Flow - Continuous or Intermittent	Continuous	Continuous	Continuous		Continuous
if Intermittent - Hrs./Yr. Flow					
Composition - Ton/Ton DMT or (Equivalent DMT)					
TPA					
Acetic Acid					
Water					
Carbon Monoxide					
Carbon Dioxide					
Oxygen					
Nitrogen					
Methyl Acetate	<.00001	~<.00001	.00107		
Xylene					00005
Propyl Acetate					
Acetaldehyde	<.00001	~<.00001	.00055		
Dimethyl Ether	.00002	~.00002	.00433		
Methyl Alcohol	.00001	~.00001	.00031		
Sulfur Dioxide					
DMT					
Metal Oxides					
Benzoic Acid					
P-Toluic Acid					
P-Carboxyl Benzaldehyde					
Hydrogen					
Misc. Light Hydrocarbons - as Methane					
Vent Stacks	Yes	Yes	Yes		Yes
Number	1	1	1		1
Height - Feet	50	100	50		30
Diameter - Inches	2	3	4		3
Exit Gas Temp. - F°	70°	70°	70°		70°
SCFM/Stack					
Type of Emission Control Device Employed	None	None	None		Condenser
Control Device I. D. No.					DT-1
Analysis					
Date or Frequency of Sampling	One Session	Never	One Session		Never
Sample Tap Location	At Vent		At Vent		
Type of Analysis	Unknown	Estimate	Unknown		Estimate
Odor Problem	No	No	No		No
Summary of Air Pollutants - T/T of DMT or (Equivalent)					
Hydrocarbons				00651	
Particulates or Aerosols					
NO_x					
SO_x					
CO				.00077	

(A) Plants 10-1 and 10-6 are part of the same overall facility.

(B) This stream never sampled, but estimated to be essentially the same as the on preceeding it in the tabulation (10-6 reactor vent).

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Plant EPA Code No.	10-6 (A)			
Product	DMT			
Capacity, Tons of DMT or (Equivalent DMT)*/Yr.	290,000			
Emissions to Atmosphere				
Stream	Crude Product "Hold-Up" Vent	Sludge Recovery Vent	Methanol Stg. & Slurry Prep. Vent	Sludge Recovery Vent
Flow - Lbs./Hr.	3	3	10,400	Unknown
Flow - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow				
Composition - Ton/Ton DMT or (Equivalent DMT)				
TPA				
Acetic Acid				
Water				
Carbon Monoxide			.00077	
Carbon Dioxide			.00102	
Oxygen			.00875	+
Nitrogen			.14086	+
Methyl Acetate				
Xylene	.00005	.00005		
Propyl Acetate				
Acetaldehyde				
Dimethyl Ether				
Methyl Alcohol				
Sulfur Dioxide				
DMT				+
Metal Oxides				
Benzoic Acid				
P-Toluic Acid				
P-Carboxyl Benzaldehyde				
Hydrogen				
Misc. Light Hydrocarbons - as Methane				
Vent Stacks	Yes	Yes	No	Yes
Number	1	1		1
Height - Feet	30	30		10
Diameter - Inches	3	3		10
Exit Gas Temp. - F°	70°	70°		70°
SCFM/Stack	10	10		
Type of Emission Control Device Employed	Scrubber	Condenser	No	Yes
Control Device I. D. No.	DT-2	DT-3		Scrubber
Analysis				DT-17
Date or Frequency of Sampling	Never	Never	Daily	Never
Sample Tap Location				
Type of Analysis	Estimate	Estimate	Orsat	None
Odor Problem	No	No	No	No
Summary of Air Pollutants - T/T of DMT or (Equivalent)		SEE OTHER SHEET		
Hydrocarbons				
Particulates or Aerosols				
NO_x				
SO_x				
CO				

(A) Plants 10-1 and 10-6 are part of the same overall facility.

TABLE DT-III
NATIONAL EMISSIONS INVENTORY
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Plant EPA Code No	10-7				
Product	DMT				
Capacity, Tons of DMT or (Equivalent)*/Yr.	180,000				
Emissions to Atmosphere					
Stream	HNO_3 Oxidizer Vent	Purification Section Vent		Emergency Vent	Air Oxidizer Vent
Flow - Lbs./Hr.	52,590	Unknown		Unknown	88,500
Flow - Continuous or Intermittent	Continuous			Intermittent	Continuous
If Intermittent - Hrs./Yr. Flow				Unknown	
Composition - Ton/Ton DMT or (Equivalent DMT)					
TPA					
Acetic Acid					
Water	.00100				.00446
Carbon Monoxide	.00163				.01471
Carbon Dioxide	.03388				.06938
Oxygen	.14771				.04538
Nitrogen	.86071				1.6875
Methyl Acetate					
Xylene					.00225
Propyl Acetate					
Acetaldehyde					
Dimethyl Ether					
Methyl Alcohol					
Sulfur Dioxide					
DMT					
Metal Oxides	NO_x = .00021				
Benzoic Acid					
Para Toluic Acid					
Para Carboxyl Benzaldehyde					
Hydrogen	NH_3 = .00017				
Misc. Light Hydrocarbons - as Methane	N_2O = .05033				
Vent Stacks	Yes	Yes		Yes	Yes
Number	1	1		2	2
Height - Feet	120	80		100	50
Diameter - Inches	24	8"		24	10
Exit Gas Temp. - F°	351				50
Flow - SCFM/Stack	10,500				9,000
Emission Control Device	Yes	Yes		No	No
Type	Catalytic Incinerator	Flare			
I. D. Number	DT-15	DT-16			
Analysis					
Date or Frequency of Sampling	Weekly (NO_x)	Never		Never	Semi-Annual
Sample Tap Location	Accessible	None			Accessible
Type of Analysis	Colorimetric				I.R.
Odor Problem	No	No		No	No
Summary of Air Pollutants T/T of DMT or (Equivalent DMT)					
Hydrocarbons			.00225		
Particulates & Aerosols			.00017		
NO_x			.00021		
SO_x					
CO			.01634		

TABLE DT-IV
CATALOG OF EMISSION CONTROL DEVICES
FOR
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Page 1 of 3

ABSORBERS/SCRUBBERS								
EPA Code No. for plant using	10-6 (1)	10-4 (2)	10-4	10-4	10-5	10-5	10-2	10-6 (1)
Flow Diagram (Fig. 1) Stream I. D.								
Device I. D. No.	DT-2	DT-4	DT-6	DT-7	DT-8	DT-9	DT-12	DT-17
Control Emission of	Aromatics	Xylene	Methanol & Xylene		H C	H C	Combustibles	Particulates
Scrubbing/Absorbing Liquid	Xylene	Solid Carbon	Water	Xylene			Water	Water
Type - Spray			X			X	X	X
Packed Column								
Column w/trays	X				X			
No. of trays					10			
Tray Type	Baffle							
Other		Fixed Bed	Plus Cond.	Venturi Scrubbers & Condensers				Plus Cyclone
Scrubbing Absorbing Liquid Rate, GPM	10	N. A.	100	180				25
Design Temp. (Operating Temp.), F°	122		(50)	338	120	190	212	(70)
Gas Rate, SCFM (Lb./Hr.)		25,000	1900		32,150	422		
T-T Height, Feet	15.3	22	16	N. A.				7.5
Diameter, Ft.	0.7	8	4	N. A.				2
Washed Gases to Stack	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Stack Height, Ft.	30	100	90	60	77	65	64	10
Stack Diameter, Inches	3	30	12	6	18	18	24	10
Installed Cost - Mat'l. & Labor - $	20,000	304,000	446,000	78,000	108,000	39,000	17,200	10,000
Installed Cost Based on - 'year' - dollars	1970	1968-1971	1970-1971	1968-1972	1971	1971	1965	1970
Installed Cost - ¢/lb. of DMT/Yr. (or/equiv. DMT)	.00345	.05067	.07433	.01300	(.02241)	(.00809)	(.01021)	.00173
Operating Cost - Annual, $ (1972)	300	116,000	129,000	10,500	89,500	116,900		900
Value of Recovered Product, $/Yr.	0	540,000	650,000	769,500	364,500	245,300		0
Net Operating Cost - Annual - $	300	-424,000	-521,000	-780,000	-275,000	-128,400		900
Net Operating Cost - ¢/lb. of DMT	.00005	Negative	Negative	Negative	Negative	Negative		.00015
Efficiency - % - SE		93.8	99.4	96.3				
Efficiency - % - SERR		93.8	99.4	96.3				

NOTES:

(1) Device DT-'N' consists of two identical scrubbers, costs indicated are for one scrubber.

(2) Unit consists of four fixed bed absorbers, costs are for entire unit.

TABLE DT-IV
CATALOG OF EMISSION CONTROL DEVICES
FOR
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Page 2 of 3

CONDENSERS		
EPA Code No. for plant using	10-6	10-6
Flow Diagram (Fig. I) Stream I. D.		
Device I. D. No.	DT-1	DT-3
Control Emission of	Xylene	Xylene
Condenser Cooling Fluid - Type	Water	Water
Rate - GPM	15	15
Temp. In - F°		
Controlled Stream - Temp. In - F°	158	158
Temp. Out - F°		
Press. In - PSIG	6 (In H_2O)	6 (In H_2O)
Length, T-T - Feet	8	8
Diameter, Inches	16	16
Tube Area - Ft.^{2}		
Installed Cost - Mat'l. & Labor - $	18,000 (A)	9,000
Installed Cost - Based on "year" - dollars	1965-1966	1969
Installed Cost - c/lb. of DMT/Yr. (or equiv. DMT)	.00310	.00155
Operating Cost - Annual - $ (1972)	1,000 (A)	500
Value of Recovered Product - $/Yr	0	0
Net Operating Cost - $/Yr.	1,000	500
Net Operating Cost - c/lb. of DMT (or equiv. DMT)	.00017	.00009
Efficiency - SE - %		
Efficiency - SERR - %		

(A) Cost of two parallel units.

TABLE DT-IV
CATALOG OF EMISSION CONTROL DEVICES
FOR
DMT AND TPA PRODUCTION
VIA
VARIOUS PROCESSES

Page 3 of 3

BAG FILTERS				
EPA Code No. for plant using	10-5	10-2	10-2	10-5 (B)
Flow Diagram (Fig. I) Stream I. D.				
Device I. D. No.	DT-10	DT-13	DT-14	DT-11
Control Emission of	TPA	TPA	TPA	Metal Oxides
Number of Compartments		3	3	
Number of Bags/Compartment				
Total Bag Area - Ft.^{2}				
Bag Cloth Material				
Design (Operating) Temp. - F°	275	(285)	(285)	
Design (Operating) Press. - PSIG	0	(0.5)	(0.5)	
Installed Cost - Mat'l. & Labor - $	29,200	222,300	250,000	348,000
Installed Cost Based on - "year" - dollars	1971	1965-1966	1966	1971
Installed Cost, ¢/lb. of DMT/Yr. (or equiv. DMT)	(.00606)	(.13194)	(.14839)	(.07220)
Operating Cost - Annual - $ - (1972)	4,900			90,800
Value of Recovered Product - $/Yr.	0			Unknown
Net Operating Cost - $/Yr.	4,900			90,800
Net Operating Cost - ¢/lb. of DMT (or equiv. DMT)	(.00102)			(.01884)
Efficiency - SE - %		100	100	
Efficiency - SERR - %		32	32	

INCINERATION DEVICES			
EPA Code No. for plant using	10-4	10-7	10-7
Flow Diagram (Fig. I) Stream I. D.			
Device I. D. No.	DT-5	DT-15	DT-16
Type of Compound Incinerated	Organic Acids & Methanol	Nitrogen Oxides	Dimethyl Ether
Type of Device - Flare			
Incinerator	X	X (Catalytic)	X
Other	w/WHB		
Material Incinerated SCFM (Lb./Hr.)	40 (GPM)	10,500	(4,550)
Auxilliary Fuel Req'd. (excl. pilot)	Yes	Yes	No
Type	Fuel Oil	NH_3	
Rate - BTU/Hr.	126 (GPH)	34 lbs./hr	
Device or Stack Height - Feet	100	120	80
Installed Cost - Mat'l. & Labor - $	750,000	131,563 (A)	118,592 (A)
Installed Cost Based on - "year" - dollars	1971-1972	1965-1972	1961-1972
Installed Cost, ¢/lb. of DMT/Yr. (or equiv. DMT)	.12500	.03655	.03294
Operating Cost - Annual - $ (1972)	163,000	114,900 (A)	11,400 (A)
Value of Heat/Steam recovered - $/Yr.	81,000	0	0
Net Operating Cost - Annual	82,000	114,900	11,400
Net Operating Cost - ¢/lb. of DMT/Yr. (or equiv. DMT)	.01367	.03192	.00317
Efficiency - % - CCR	99+	85	
Efficiency - % - SERR		85	

NOTES: (A) Cost of two parallel units.

(B) Device is referred to as precipitator, but no descriptive details or specifications are reported.

TABLE DT-V
NUMBER OF NEW PLANTS BY 1980

Current* Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
2,865	300	2,565	5,900	5,900	2,335	300	7 - 8

NOTE: All capacities in MM lbs./yr.

*TPA and DMT, expressed as equivalent DMT.

TABLE DT-VI
WEIGHTED EMISSION RATES

Chemical TPA and DMT

Process Xylene Oxidation

Increased Capacity by 1980 2,335

Pollutant	Emissions Lb./Lb.*	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions Lbs./Year
Hydrocarbons	.03162	73.83	80	5,907
Particulates	.00047	1.10	60	66
NO_x	.00003	.07	40	3
SO	.00036	.84	20	17
CO	.01836	42.87	1	43
			Significant Emission Index =	6,036

*Emissions based on assumption that 40% of new capacity to be based on Amoco process and 15% based on each of four other processes utilized in U. S. today, as summarized in Table DT-III.

Ethylene

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I. Introduction

Ethylene is, today, the pre-eminent petrochemical in the United States; both in terms of quantity and value. More than 20 billion pounds will have been produced in 1972. Of this, approximately 15 billion pounds is produced by the steam cracking process, the method which is the subject of this report. The balance has its origin as by-product from a variety of refinery operations and processes. Of the 15 billion pounds, about 80% is derived from ethane and propane, the remainder from butane, field condensate, naphtha and gas oil. Most of the air emissions associated with the production of ethylene result from either of two "operations": (1) The removal of acid gases (CO_2 & H_2S) from the cracked gas and (2) Hydrocarbon venting and/or flaring during plant start-ups and emergencies. In addition to the vapor emissions, quanitites of waste water and spent caustic are produced. Also some plants (generally the naphtha-crackers) produce a heavy, hydrocarbon, tar-like substance which, if incinerated, would add to the volume of air emissions produced. In general, however, air emissions from ethylene are relatively low.

By 1980 it is expected that the demand for ethylene in the United States will approach 40 billion pounds per year (1). The required new capacity will be based increasingly on heavier feed stocks - naphthas and gas oils. As a result proportionately greater quantities of sulfur compounds and "tar" will have to be disposed of by the industry in the future.

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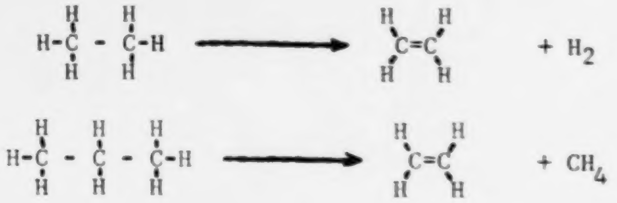
(1) C.E.P. Vol. 68, No. 9.

II. Process Description

Ethylene is produced primarily by the pyrolysis of hydrocarbons. In the United States ethane and propane currently predominate as feed stock material. The chemical reaction for their pyrolysis is:



$$H_3C-CH_3 \longrightarrow H_2C=CH_2 + H_2$$

$$H_3C-CH_2-CH_3 \longrightarrow H_2C=CH_2 + CH_4$$

The conversion or "cracking" of the feed stock takes place within the tubes of the cracking furnace. The reaction is initiated at about 1100° F. Normal temperatures within the cracking section of the heater are 1500 to 1600° F with a residence time of one second or less. Yields and conversion vary with the feed stock and the desired product mix. Typically a unit cracking ethane might operate at a severity such that 60% of the ethane is cracked, ultimate yield of ethylene will be about 80%. Naphtha cracking, on the other hand, would yield only about 30% ethylene. The hydrocarbon feed stock, whatever its nature, is always diluted with steam to depress coking tendencies within the furnace tubes.

In order that only the desired degree of cracking be obtained it is necessary to control the temperature - residence time parameter very closely. This requires that the hot effluent gases from the furnace be cooled rapidly to a temperature which will 'quench' the cracking reaction. Consequently the cracked gases from the furnace are cooled in a variety of ways; but usually at some point by direct contact with water in the "quench tower". Increasing use is being made of transfer line waste heat boilers up-stream of the quench tower to recover some of the large amounts of heat that are removed from the cracked gas during the quench.

The purification and separation of the various products and by-products constitute a major element in the manufacturing process. They are accomplished in a variety of ways depending on the feed stock, age of the plant, contractor and many other factors. Accordingly it must be realized that the following description of that section of the process pertains to only one of many configurations extant:

Subsequent to quenching the cracked gases are compressed prior to treatment for removal of the contained acid gases (CO_2 & H_2S). The acid gases are usually absorbed by some combination of systems using monoethanol amine (MEA), caustic and water. After desorption, the contaminants are usually vented or burned. The purified gas stream is then dried and further compressed before fractionation.

After compression, the cracked gas is cooled to cryogenic temperatures and hydrogen is flashed off and sent to either additional purification facilities or to fuel. The dehyrogenated stream flows to the demethanator where overhead methane is sent to fuel and the C_2^+ bottoms are pressured to the de-ethanizer.

From the de-ethanizer the C_3^+ bottoms are sent to the de-propanizer while the overhead is selectively hydrogenated in the 'light acetylene converter', in order to remove trace amounts of acetylene. The stream then goes to the ethylene splitter where the ethylene and ethane are separated. Ethane is recycled to the cracking furnace. The overhead from the ethylene splitter is final product and is sent to storage or pipeline.

The C_4^+ depropanizer bottoms are sent to the debutanizer while the overhead is selectively hydrogenated in the 'heavy acetylene splitter' in order to remove trace amounts of methyl acetylene and propadiene. It then goes to the propylene splitter where the propane and propylene are separated. Propane is usually recycled to the cracking furnace. The overhead from the propylene splitter is pressured to storage spheres or pipeline.

The final tower in the described fractionation train is the debutanizer where various C_4 compounds are separated from the dripolene or pyrolysis gasoline fraction. This C_5^+ material may be rejected as waste or, after hydrogenation, may be used as gasoline blending stock or a source of aromatics.

III. Plant Emissions

A. Continuous Air Emissions

1. Cracking Furnace Combustion Stack

All ethylene plant operators report the use of "sweet" natural gas supplemented by varing amounts of plant produced sulfur-free fuel gas to fire their cracking furnaces. The plant produced fuel is generally a mixture of hydrogen and methane. The sulfur content of the imported fuel varies from "nil" to "less than 1 grain/100 SCF." The unit reporting the highest sulfur consumes 1.0 x 10^9 lb./yr. of imported fuel in the production of 1.2 x 10^9 lb./yr. of ethylene. The emission rate is 10,000 lb./yr. of sulfur. As SO_2, this is less than 2 x 10^{-5} tons/ton of ethylene.

2. Waste Water and Spent Caustic De-Gassing

Most producers of ethylene "de-gas" waste quench water, waste wash water (from the caustic-water wash column) and spent caustic prior to recycling or further processing these liquid streams. The desorbed gases are either returned to the process, vented, flared or sent to a pollution control device. These emissions are summarized in Table III.

3. "Acid Gas Removal" Vents

So-called 'Acid Gas' (H_2S & CO_2) is removed from the furnace effluent gases by either caustic washing or contact with a regenerable absorbent such as MEA. The spent liquor from the former method is generally neutralized before disposal. The neutralization regenerates the hydrogen sulfide, and results in its evolution from the neutralized liquid waste. The hydrogen sulfide is either vented to atmosphere - as reported by the operator of EPA coded plant 11-1 - or burned. The hydrogen sulfide from the regenerable absorbent is reported as being generally burned, although one operator (EPA Code 11-9) sends it to a Claus plant. The emissions from the acid gas removal section constitute one of the primary sources of air pollution from the ethylene process. Of those sulfur bearing, 'acid gas' vent streams reported as being (eventually) vented to the atmosphere, the highest emission rate - as SO_2 - is .0012 ton/ton of ethylene. The vent streams reported for this section are summarized in Table III.

4. Plant Flare

Most ethylene plants deploy a continuously lighted plant flare. Normally only pilot fuel gas and flare sweep gases are burned and there are no noxious emissions. However, during plant emergencies this may not be the case - see section III - B, "Intermittent Air Emissions".

5. Storage Losses

With the exception of the relatively small amounts of C_5^+ gasoline and heavy tars all ethylene feed stocks and products are stored under pressure. So there are no continuous vent losses. This does not apply, of course, to the two operators (EPA Codes 11-9 and 11-10) who crack naphtha, their feed stock storage tanks utilize, respectively, nitrogen blanketing and a floating roof.

B. Intermittent Air Emissions

1. Cracking Furnace Decoking

Periodically, the process side of the cracking furnace requires decoking. Several operators reported emissions from this operation and they are summarized in Table III. It should be presumed that all operators of ethylene cracking furnace require a similar operation.

2. Acetylene Converter Regeneration

Periodically, the 'Light Acetylene Converter', or acetylene hydrogenation reactor, and the 'Heavy Acetylene Converter', or methyl acetylene and propadiene hydrogenation reactor, require regeneration. Several operators reported emissions from this operation and they are summarized in Table III. It should be presumed that nearly all ethylene plants employ and regenerate a light acetylene converter, but some may not utilize a heavy acetylene converter. Since acetylene can be selectively adsorbed in solvents such as DMF*, some operators may use a scrubbing technique for its removal.

3. Start-up and Emergency Vents

This type of emission is universally encountered in the petrochemical industry and will vary from process-to-process, from operator-to-operator and even from year-to-year. One operator (EPA Code No. 11-13) estimates that 1.49% (8.9×10^6 lbs.) of his production will be flared during 1973 due to process upsets and a major plant turnaround. Other estimates of emissions in this category are listed in Table III.

C. Continuous Liquid Wastes

1. Process Tar

Not all operators report tar formation. Considerably higher amounts of tar are reported by the operators who crack naphtha. Operator 11-10 reports 35,000 lbs./hr. or 0.5 tons of tar/ton of ethylene product. The highest amount of tar reported by a non-naphtha cracker is 100 lbs./hr. or .001 tons/ton of ethylene. In general the disposal method is not specified, although one operator (EPA Code 11-2) reports that it is used as a sanitary land fill.

2. Cracking Furnace Steam Condensate

The condensate from cracking furnace dilution steam is sent to the waste water treatment facilities of a few operators. The amount varies from plant to plant but is measured in hundreds of gallons per minute.

3. Quench Water

Some operators treat their used quench water as waste; however, the literature reports that the newer plants generate steam from the quench water. Those operators that do report this stream as waste indicate that its flow rate is measured in hundreds of gallons per minute.

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*di-methyl formamide

4. Boiler and Cooling Tower Blow-Down

Three operators reported a continuous boiler and cooling tower blow-down. One large plant operator (EPA Code 11-13) reported that the combined flow of these two waste water streams was 935 GPM. The other two operators reported about half of that amount.

5. Spent Caustic

Several operators report the use of caustic in removing acid gases from the cracking furnace effluent stream. One operator (EPA Code 11-13) reports a continuous flow of waste caustic to a neutralizing pond. The quantity of caustic is unreported as is the ultimate pond disposal method. Operators EPA 11-5 and 11-8 report spent caustic rates of 20 and 16 GPM respectively; however, they do not specify how this waste is treated. Presumably all operators use either caustic or MEA* (or caustic and MEA) in their acid gas removal section; consequently many will have spent caustic for disposal.

6. Wash Water

Three operators report the use of a water wash subsequent to the caustic wash step in the acid gas removal section of the plant. The quantity of wash water used and the method of its ultimate disposal are not reported.

D. Intermittent Liquid Wastes

1. Acetylene Converter Regeneration

Several operators report the use of direct contact condensers and/or water scrubbers on the effluent gases from the acetylene converter regeneration. Although the flow rate may be quite high - operator EPA Code 11-5 reports 1500 GPM, - the total volume of waste water is relatively small because the converters require regeneration only about twice a year. The duration of a given regeneration is normally limited to a few days.

2. Cracking Furnace Decoking

It is presumed that all operators decoke their cracking furnaces regularly. Three operators water scrub the coke bearing gases discharged during this operation. One operator (EPA Code 11-5) reports generating 1500 GPM of waste water as a result of this activity. However, again, the total volume of waste water is relatively small due to the infrequency of the operation.

3. Drier Column Water

It may be presumed that most or all operators dry the cracked gas subsequent to its treatment in the acid gas removal section. It has not been reported whether the removed water is rejected continuously or intermittently; nor has its rate been reported. Such waste water streams, small though they may be, most probably exist even though they have not been reported.

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*mono-ethanol amine

E. Solid Wastes

Solid wastes from the process consist primarily of desiccants and furnace coke. Only one operator (EPA Code 11-13) made an estimate of these. However, two operators reported quantities (@ 1000 lb./day) of unspecified solid waste materials. Operator EPA Code 11-13 reports the disposal of 66,000 lb./yr. of spent desiccants and 5000 lb./yr. of coke, both materials being used as sanitary land fill.

F. Odors

In general, the steam cracking of hydrocarbons to produce ethylene does not appear to be a process that has an "odor problem".

Only one respondent (EPA Code 11-1) reported an odor complaint in the past year and that was due to a flare failure. Most of the reported odors are said to be detected only on the plant property and most of those are intermittent. The odoriferous materials are usually either hydrogen sulfide or unidentified compounds contained in the heavy by-product streams that the process produces.

Operators of steam crackers seem to have eliminated most odors by means of extensive use of flare systems on gaseous hydrocarbon waste and vent streams.

The continuous sources of odors are degassing of quench water, and disposal of spent caustic. According to the questionnaires, these operations are typically well enough controlled to avoid odor problems. The intermittent sources of odors are furnace decoking, steaming out of driers, regeneration of hydrogenation catalyst and flare failure.

In the future, the increased use of heavier feedstocks will result in increase production of odoriferous by-product hydrocarbons and hydrogen sulfide. However, on the basis of the previous attention paid by the industry to this kind of detail, it seems safe to assume that except for the unavoidable occasional equipment failure, the process will continue to be one that operates without "odor problems"

G. Fugitive Emissions

All respondents to the questionnaire reported little or no air pollution resulting from fugitive emissions. There was fairly general agreement that these can be and are minimized by following good maintenance practices and procedures. In most instances, replies were qualitative, but where quantities are given, they are usually estimates. A few of the replies were (in part):

> "Process material balance closure averages 0.5% low but much of this is believed to be metering error".

> "Approximately 20,000 lbs./year fugitive hydrocarbons from small leaks. Engineering estimate".

> "Approximately 80 SCFH vents to atmosphere from on-line process analyzers in various parts of the plant. These streams contain H_2, C_1 - C_5 hydrocarbons and H_2S".

The most comprehensive leakage estimate was given by the company with EPA Code 11-11 and it can be summarized as follows:

Source	Estimated Losses, lbs./year
Pump Seals	53,500
Control & Manual Valves	131,000
Safety Valves Vented to Atmosphere	35,000
Unit Leaks	103,500
Compressor Seals	
Ejectors	
Total	323,000

This unit has a capacity of 395,000,000 lbs./year of ethylene, giving a fugitive emission rate of about 0.0008 lbs./lb. of ethylene. However, it is a unit with gas oil feed so produces a wide range of other products. Thus, if calculated on a different basis, the fugitive emission rate is about 0.00015 lbs./lb. of fresh feed.

The most comprehensive qualitative list of fugitive emission sources was given by the company with EPA Code 11-3 and it can be summarized as follows:

1. Fuel gas vent resulting from a low gas pressure automatic shutdown of a cracking furnace.
2. Vapors from oil filter on waste water stream.
3. Vapors from decanted water.
4. Light oil storage drum vapors.
5. Heavy oil vapors from processing, storage or loading.
6. Control gas vent from flare stack, pneumatic instruments which are fuel gas rather than air-operated.
7. Pump seal and packing leakage.
8. Vapors from engine crankcases and compressor oil reservoirs.
9. Losses while purging and filling sample containers.
10. Vents from moisture analyzers and gas chromatographs.
11. Vapors from oil drainage for maintenance.
12. Vapors from equipment purge both before and after maintenance.

In addition to these, as mentioned in other replies are:

1. Valve packing leaks.
2. Flange leaks.
3. Compressor seal leaks.

In summary, there are many potential sources of fugitive emissions from the steam cracking process. However, it appears as if the industry holds these to a relatively small total by means of careful design and timely maintenance. It seems reasonable to expect that future operations will continue to try to minimize losses because of economic considerations. However, it must be remembered that by 1980 this will be a 40 billion pound per year industry so that even a fugitive emission loss as low as 0.01% will result in 4,000,000 pounds per year of hydrocarbon emissions. Consequently, constant attention to the potential problem is essential.

IV. Emission Control

The various emission control devices that are employed by operators of ethylene plants are summarized in the Catalog of Emission Control Devices, Table IV. Unfortunately, in only a few instances, are sufficient data available to permit calculation of device efficiency. Never-the less, certain generalizations about the performance of the devices utilized can be made:

Water Scrubbers

In ethylene production these devices are used to either prevent or reduce the emission of coke particles during furnace decoking or to prevent or reduce the emission of catalyst fines and desorbed hydrocarbon vapors during converter regeneration. One operator (EPA Code No. 11-13) states that his scrubber is able to remove 99% of the furnace coke particles larger than 2 microns; the overall efficiency of that device (EL-10) is calculated to be 98%. The scrubbers should be nearly as effective in the direct contact condensation of the relatively heavy hydrocarbons ("Green Oil") that are evolved during converter regeneration. In general one would expect that properly designed and operated water scrubbers would be 90 + % effective in the described ethylene plant service.

Incinerators and Flares

Most ethylene plants employ at least one flare or incinerator. When 'straight' hydrocarbons are being burned, they are very efficient pollution control devices. However, when sulfur or halogens are present in the stream being flared, it is more difficult to characterize device performance. Accordingly, devices in this category have been assigned two efficiencies. One, "CCR", is a measure of completeness of combustion; the other , "SERR", is a measure of the reduction of pollutant concentration on a weighted basis. These efficiencies, and other pertinent data are tabulated in Table IV. A complete discussion of "CCR" and "SERR" efficiencies may be found in Appendix V of this report.

Most ethylene plant operators report using John Zink smokeless flares, ranging in size from 24" to 48". Flare capacities (smokeless) average about double plant ethylene capacities; that is,a plant producing 75,000 lb./hr. of ethylene has (on the average) a flare with a capacity for burning 150,000 lb./hr. of hydrocarbons - smokelessly. Operator EPA Code No. 11-7 states that, for his flare system, smokeless operation requires a steam injection rate of about 8000 lb. of steam per MM BTU of heat release. In addition to promoting smokeless buring, steam injection also reduces NO emissions by lowering flame temperatures.

Unfortunately, very little quantitative information on flare and/or incinerator efficiency was provided by the questionnaire respondents. One would expect, however, that "CCR" efficiencies will average close to 100% while "SERR" efficiencies will vary widely - depending on the stream being 'treated'.

K. O. Drums, Demisters & De-Gassers

This type of device is used primarily, in ethylene plant service, to desorb and separate hydrocarbon gases from various waste streams - principally spent caustic and wash water. The efficiency of the device ('De-gasser') is dependent to a very large extent on the amount of gas 'held' by the liquid; which in turn is related to operating temperatures and pressures. These conditions are not disclosed, however, one may speculate that relatively small amounts of gas are left in these streams since they would directly (and adversly) affect overall plant yield.

It is unlikely that any change in operating conditions can be made that will reduce air emissions since yield and selectivity are not directly related to the two primary sources of air pollution. (See Section I)

Air emissions could be significantly reduced by the use of purer (less sulfur) feed stocks. Unfortunately it is generally agreed that feed stocks will contain increasing amount of sulfur as ethylene plant operators gradually change to heavier feed. One operator (EPA Code No. 11-10) states that plants using refinery gas oil as feed would produce three to six times as much sulfur dioxide as a plant using lighter (Gulf Coast field condensate) feed.

Development work directed toward reductions in emissions from this process falls into the following general categories:

(1) Economical sulfur recover from small sulfur bearing streams.

(2) Prevention of hydrocarbon venting to atmosphere rather than to flare.

(3) More efficient design and operation of devices currently being utilized.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. Although the growth rate of ethylene production by pyrolysis is forecast to be significant, the emission data indicate that the quantity of pollutants emitted to the atmosphere is less, on a weighted basis, than from many of the other processes that are currently being surveyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Tables V, VI, and VII.

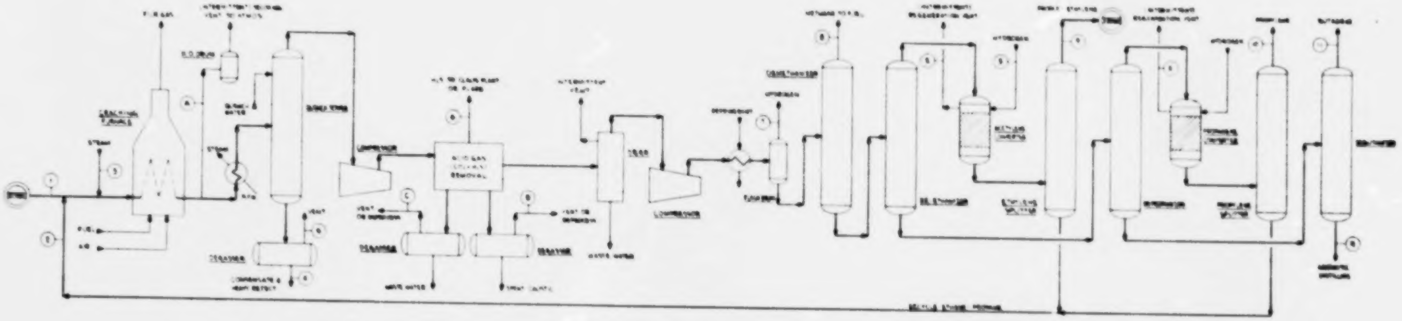
Support for the Table V forecast of new plants has appeared in print as recently as September, 1972 (Chemical Engineering Progress, pp 92-98). This article indicates that about 20 new billion lbs./year plants will have to be constructed between now and 1980 to keep up with the estimated demand. Thus, the number of new units to be built, especially when the size of each unit is considered, is certainly significant.

However, on a weighted emission basis, a Significant Emission Index (SEI) of 2,431 has been calculated in Table VII. This is substantially less than the SEI's that have been calculated for other processes in the study. Hence, the recommendation to exclude an in-depth study on ethylene production from the scope of work.

VI. ETHYLENE PRODUCERS

The following tabulation of producers of ethylene indicates published production capacity:

Company	Location	Capacity - MM Lb./Yr.
Allied/Wyandotte	Geismar, La.	600
Arco	Wilmington, Calif.	100
Chemplex	Clinton, Ohio	500
Citgo	Lake Charles, La.	440
Conoco	Lake Charles, La.	550
Dow	Bay City, Mich.	170
	Freeport, Texas	1,500
	Plaquemine, La.	900
Du Pont	Orange, Texas	750
Eastman Kodak	Longview, Texas	800
El Paso Products	Odessa, Texas	500
Enjay	Baton Rouge, La.	1,900
	Baytown, Texas	90
	Bayway, N. J.	225
Goodrich	Calvert City, Ky.	250
Gulf Oil	Cedar Bayou, Texas	400
	Port Arthur, Texas	925
Jefferson	Port Neches, Texas	500
Mobil	Beaumont, Texas	470
Monsanto	Alvin, Texas	650
	Texas City, Texas	150
National Distillers	Tuscola, Ill.	350
Northern Petrochem.	East Morris, Ill.	800
Olin	Brandenburg, Ky.	100
Phillips	Sweeny, Texas	600
Phillips/Houston Nat. Gas	Sweeny, Texas	500
Shell	Deer Park, Texas	1,450
	Norco, La.	500
Sinclair-Koppers	Houston, Texas	500
Sunolin	Claymont, Del.	225
Union Carbide	Seadrift, Texas	1,200
	Taft, La.	500
	Texas City, Texas	1,200
	Torrance, Calif.	150
	Whiting, Ind.	150
Columbia Carbon	Lake Charles, La.	900
Northern Natural Gas	Bushton, Kansas	800
	Total	22,295


FUEL GAS
INTERMITTENT DECOKING VENT TO ATMOS.
CRACKING FURNACE
STEAM
FUEL
AIR
QUENCH WATER
QUENCH TOWER
DECANTER
CONDENSATE & HEAVY DISTILLATE
VENT
COMPRESSOR
ACID GAS REMOVAL
H₂S TO CLAUS PLANT OR FLARE
VENT OR INCINERATION
DECANTER
WASTE WATER
SPENT CAUSTIC
VENT TO INCINERATION
INTERMITTENT VENT
DRYER
WASTE WATER
COMPRESSOR
REFRIGERANT
HYDROGEN
FLASH DRUM
METHANE TO FUEL
DEMETHANIZER
DE-ETHANIZER
INTERMITTENT REGENERATION VENT
HYDROGEN
ACETYLENE CONVERTER
PRODUCT ETHYLENE
ETHYLENE SPLITTER
DEPROPANIZER
INTERMITTENT REGENERATION VENT
HYDROGEN
PROPADIENE CONVERTER
PROPYLENE
PROPYLENE SPLITTER
BUTADIENE
DEBUTANIZER
AROMATIC DISTILLATE
RECYCLE ETHANE PROPANE

*NOTE

THE PROCESSING SCHEME WILL VARY WITH THE COMPOSITION AND QUALITY OF THE FEED STOCK — AND FROM PLANT TO PLANT. MANY OF THE PROCESSING SUB-SECTIONS WHICH COMPRISE THE ETHYLENE PLANT MAY BE EXPANDED OR DELETED IN ANY GIVEN INSTALLATION. THE FLOW DIAGRAM DEPICTS ONE OF THE MANY ALTERNATE SCHEMES AVAILABLE.

CIRCLED NUMBERS (1) REFER TO MATERIAL BALANCE STREAMS.
CIRCLED LETTERS (A) REFER TO [illegible] [illegible] STREAMS.

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0190

R-204

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TABLE El-1
TYPICAL ETHYLENE UNIT
MATERIAL BALANCE, T/T OF ETHYLENE

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
Component	Fresh Feed	Recycle Feed	Steam to Reactor	Condensate and Heavy Reject	Hydrogen to Acetylene Converter	Reject Acid Gas (b)	Hydrogen Vent Gas	Demethanizer Overhead	Ethylene Product	Propylene Product	C_4's Product	C_5^+ Gasoline
H_2					.0008		.0589	.0065				
H_2S						.0002						
CO_2						.0005						
C_1					.0001		.1154	.0956	.0003			
C_2H_2												
$C_2^=$							.0020	.0030	1.0000			
C_2	.9859	.5749					.0011	.0011	.0005	.0020		
C_3H_4												
$C_3^=$										.0988		
C_3	.4943	.0353								.0040	.0002	
$C_4^{==}$											.0205	
$C_4^=$											.0114	
C_4											.0020	.0002
C_5/iC_6											.0004	.0079
C_6-C_8												.0099
BZ												.0278
TOL												.0055
XYL												.0047
C_9^+				.0007								.0006
Sulfur	.0002 (a)											
H_2O			0.6271	0.6271								
	1.4804	.6102	0.6271	0.6278	.0009	.0007	0.1774	.1062	1.0008	.1048	.0345	.0566

(a) Assumes feed contains 150 ppm sulfur.

(b) Assumes regenerative amine type scrubber. A caustic type removal unit can also be employed.

TABLE EL-II
ETHYLENE
VIA
LIGHT HYDROCARBON PYROLYSIS
GROSS HEAT BALANCE

Heat Out		BTU/lb. of ethylene produced
Endothermic heat of reaction		2181*
Furnace effluent quench (including heat exchange)		2343
Furnace effluent final condensation and cooling		1125
Heat to furnace economizing devices		1526
Heat losses and inefficiencies		1129
	Total	8304
Heat In		
Fuel to cracking furnace		7630
Steam to cracking furnace		674
	Total	8304**

*Feed stock = 100% ethane w/ethane conversion @ 65%

**Depending on feed stock composition, cracking severity, furnace design, etc. - this duty can range from 7,000 to 10,000 BTU/lb. of ethylene.

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Page 1 of 13

Company					
Location					
EPA Code Number		11-1			
Date on-stream					
Capacity - Tons of Ethylene/Yr.		600,000			
Average Production - Ethylene. T/Yr.		540,000			
Range in Production - % of Max. (f)		5			
Emissions to Atmosphere					
Stream	Propane Vaporizer Vent	Quench Water Off-gas	Emergency Vent	CO_2 Vent Ex Gas Purif. Section	Flare Sweep Gas
Flow - Lb./Hr.	<1	2850	15,000	1,025	720 (e)
Flow Characteristic - Continuous/Intermittent	Intermittent	Continuous	Intermittent	Continuous	Continuous
If Intermittent - Hrs./Yr. of Flow	340		0.05		
Composition - Tons/Ton Ethylene					(After Burning)
Hydrogen			<.00001		
Methane			<.00001		
Ethane	<.00001	<.00001	<.00001		
Ethene		<.00001	<.00001		
Propane	<.00001		<.00001		
Propene	<.00001		<.00001		
C_4^+ Hydrocarbons	<.00001	<.00001	<.00001		
Acetylene			<.00001		
Oxygen					
Nitrogen					
Carbon Monoxide		<.00001			
Carbon Dioxide				.00749	.01356
Nitrogen Oxide					
Sulfur Oxides					
Hydrogen Sulfide					
Water		.0208			.01132
Sample Tap Location	C_3 Storage Tank	Not Specified	Source Stream	Not Sampled	Not Specified
Date or Frequency of Sampling		1971	Source - 15 Min.		Every 15 Min.
Type of Analysis	GLC	Not Specified	GLC	Assumed	GLC
Odor Problem	No	No	Yes	No	No
Vent Stacks					
Flow, SCFM Per Stack	.008	111	7,000	146	284
Number	1	9	1		1
Height - Feet	30'	12'	100'		240'
Diameter - Inches	2"	8"	30"		30"
Exit Gas Temperature - F°	- 40	194	113		Ambient
Emission Control Devices	No	No	No		Yes
Type - Flare					X
Water Scrubber					
Refrigerated Condenser & F. O. Drum					
Other					
Catalog I. D. Number					EL - 22
Total Hydrocarbon Emissions - Ton/Ton of Ethylene (g)			<.00001		
Total Particulate/Aerosol Emissions - Ton/Ton of Ethylene					
Total NO_x					
Total SO_x					
Total CO			<.00001		

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Page 2 of 13

Company			
Location			
EPA Code Number	11-2		
Date on-stream			
Capacity - Tons of Ethylene/Yr.	385.000		
Average Production - Ethylene, T/Yr.			
Range in Production - % of Max. (f)	0		
Emissions to Atmosphere			
Stream	Acid Gas Vent	Distillation Emergency Vent	Miscellaneous Leaks
Flow - Lb./Hr.	9,180 (a)	800,000 (a)	20,000/Yr.
Flow Characteristic - Continuous/Intermittent	Continuous	Intermittent	Intermittent
if Intermittent - Hrs./Yr. of Flow		Not Specified	Not Specified
Composition - Tons/Ton Ethylene	(After Burning)	(After Burning)	
Hydrogen		Not Specified	
Methane			
Ethane			
Ethene			.00003
Propane			
Propene			
C_4^+ Hydrocarbons			
Acetylene			
Oxygen			
Nitrogen			
Carbon Monoxide			
Carbon Dioxide	.22201		
Nitrogen Oxide			
Sulfur Oxides	.00065		
Hydrogen Sulfide			
Water	.15835		
Sample Tap Location	None	None	None
Date or Frequency of Sampling			N. A
Type of Analysis	Calculated		None
Odor Problem	No	No	
Vent Stacks			
Flow, SCFM Per Stack	Not Specified		
Number	1		0
Height - Feet	120'		
Diameter - Inches	42 @ Tip		
Exit Gas Temperature - F°	1600		
Emission Control Devices	Yes		
Type - Flare	X		
Water Scrubber			
Refrigerated Condenser & K. O. Drum			
Other			
Catalog I. D. Number			
Total Hydrocarbon Emissions - Ton/Ton of Ethylene (g)		.00003	
Total Particulate/Aerosol Emissions - Ton/Ton of Ethylene			
Total NO_x			
Total SO_x		.00065	
Total CO			

EL - 18

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Page 3 of 13

Company					
Location					
EPA Code Number	11-4		11-5	11-7	11-8
Date on-stream					
Capacity - Tons of Ethylene/Yr.	145,000		450,000	325,000	[illegible]7,500
Average Production - Ethylene Tons/Yr.				325,000	
Range in Production - % of Max. (f)	25		0	18	0
Emissions to Atmosphere					
Stream	Emergency Vent Prod. Fract.	Emergency Vent Prod. Fract.	Emergency Vent Methanator	Plant Flare System	Plant Flare System
Flow - Lbs./Hr.	(a) 36,000 (Max.)	(a) 36,000 (Max.)	34 Lb./Yr.	(a) 5,740 (Avg.)	Not Specified ↓
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Intermittent	Continuous	
if Intermittent - Hrs./Yr. Flow	Not Specified	Not Specified	Not Specified		
Composition - Tons/Ton of Ethylene	After Burning	After Burning		After Burning	
Hydrogen			∠.00001		
Methane			∠.00001		
Ethane			∠.00001		
Ethene			∠.00001		
Propane					
Propene					
C_4+ Hydrocarbons					
Acetylene					
Oxygen					
Nitrogen			∠.00001	.00373	
Carbon Monoxide	∠.00001	∠.00001	∠.00001		
Carbon Dioxide	Not Specified	Not Specified		.18298	
Nitrogen Oxides	.00001	.00001			
Sulfur Oxides					
Hydrogen Sulfide					
Water	Not Specified (coke) ∠.0001	Not Specified (coke) ∠.00001		.10466	
Sample Tap Location			None		
Date or Frequency of Sampling	Weekly	Weekly		Twice Month	
Type of Analysis	GLC	GLC	Calculated	GLC	↓
Odor Problem	No	No	No	No	No
Vent Stacks	Yes	Yes	Not Specified	Yes	Yes
Flow, SCFM Per Stack	Not Specified	Not Specified	↓	1500	Not Specified
Number	1	1		1	1
Height - Feet	Ground Level	Ground Level		225	200
Diameter - Inches				36	24 @ Tip
Exit Gas Temperatures - F°				400	
Emission Control Devices	Yes	Yes	No	Yes	Yes
Type - Flare	Y	X		X	X
Water Scrubber					
Refrigerated Condenser & F. O. Drum					
Other	X Smoke Suppressor	X Smoke Suppressor			
Catalog I. D. Number	EL - 23	EL -23		EL - 20	EL - 21
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)			∠.00001		Not Specified ↓
Total Particulate & Aerosol Emissions Ton/Ton Ethylene	∠.00001				
Total NO_x	.00002				
Total SO_x					
Total CO	.00001		∠.00001		

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Page 4 of 13

Company			
Location			
EPA Code Number	11-6		
Date on-stream			
Capacity - Tons of Ethylene/Yr.	100,000		
Average Production - Ethylene Tons/Yr.			
Range in Production - % of Max. (f)	0		
Emissions to Atmosphere			
Stream	(h)		Flare Vent
Flow - Lbs./Hr.	Unspecified		Unspecified
Flow Characteristic - Continuous or Intermittent	Intermittent		Continuous
if Intermittent - Hrs./Yr. Flow	Unspecified		
Composition - Tons/Ton of Ethylene			
Hydrogen			
Methane			
Ethane			
Ethene			
Propane			
Propene			
C_4 + Hydrocarbons			
Acetylene			
Oxygen	+		+
Nitrogen	+		+
Carbon Monoxide			
Carbon Dioxide	+		+
Nitrogen Oxides			
Sulfur Oxides			
Hydrogen Sulfide			
Water	+		+
Sample Tap Location	One is provided		None
Date or Frequency of Sampling	None		
Type of Analysis	None		
Odor Problem	None		Unspecified
Vent Stacks			
Flow, SCFM Per Stack	Unspecified		Unspecified
Number	1		
Height - Feet	12 above scrubber		
Diameter - Inches	6		
Exit Gas Temperatures - F°	212		
Emission Control Devices	Yes		Yes
Type - Flare			+
Water Scrubber	+		
Refrigerated Condenser & K. O. Drum			
Other			
Catalog I. D. Number	EL-31		EL-32
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)		None	
Total Particulate & Aerosol Emissions Ton/Ton Ethylene		None	
Total NO_x		None	
Total SO_x		None	
Total CO		None	

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Company			
Location			
EPA Code Number		11-9	
Date on-stream			
Capacity - Tons of Ethylene/Yr.		600,000	
Average Production - Ethylene Tons/Yr.		600,000	
Range in Production - % of Max. (f)		0	
Emissions to Atmosphere		(b)	
Stream	Plant Flare System	Hydrogenation Catalyst Regeneration Vent	Acid Gas Vent
Flow - Lbs./Hr.	9,000	8,150	1800 - 2600
Flow Characteristic - Continuous or Intermittent	Continuous	Intermittent	Continuous
If Intermittent - Hrs./Yr. Flow		216	
Composition - Tons/Ton of Ethylene	After Burning	Not Specified	(c)
Hydrogen		↓	
Methane			
Ethane			
Ethene			
Propane			
Propene			
C_4^+ Hydrocarbons			
Acetylene			
Oxygen			
Nitrogen	.00504		
Carbon Monoxide			
Carbon Dioxide	.02374		.00492
Nitrogen Oxides			
Sulfur Oxides			
Hydrogen Sulfide			.00820
Water	.06799		.00028
			C_1 to C_7 HC .00197
Sample Tap Location	None	None	Not Specified
Date or Frequency of Sampling		Not Sampled	Not Specified
Type of Analysis			Mass Spec.
Odor Problem	No		No
Vent Stacks	Yes	Yes	Not Specified
Flow - SCFM Per Stack		300,000 (d)	↓
Number	1	1	
Height - Feet	360	260	
Diameter - Inches	60	192	
Exit Gas Temperatures - F°	1,000	260 - 300	
Emission Control Devices	Yes	Yes	Yes
Type - Flare	X		
Water Scrubber			
Refrigerated Condenser & K. O. Drum			
Other		X K. O. Drum	X Claus Unit
Catalog I. D. Number	EL - 17	EL - 12	N. A.
Total Hydrocarbon Emissions - Ton/Ton Ethylene (e)		Cannot be Determined	
Total Particulate & Aerosol Emissions Ton/Ton Ethylene		↓	
Total NO_x			
Total SO_x			
Total CO			

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company				
Location				
EPA Code Number	11-10			
Date on-stream				
Capacity - Tons of Ethylene/Yr.	330,000			
Average Production - Ethylene Tons/Yr.				
Range in Production - % of Max. $^{(f)}$	0			
Emissions to Atmosphere				
Stream	Vent From Furnace Decoking	**Acid Gas** Vent	**Demethanizer** Emergency Vent	C_2 Splitter **Emergency Vent**
Flow - Lbs./Hr.	3,179	Not Specified	505 Ton/Yr.	358 Ton/Yr.
Flow Characteristic - Continuous/Intermittent	Intermittent	Continuous	Intermittent	Intermittent
if Intermittent - Hrs./Yr. Flow	Not Specified		Not Specified	Not Specified
Composition - Tons/Ton of Ethylene		Not Specified except SO_2		
Hydrogen				
Methane				
Ethane				
Ethene				
Propane				
Propene				
C_4^+ Hydrocarbons				
Acetylene				
Oxygen				
Nitrogen				
Carbon Monoxide				
Carbon Dioxide				
Nitrogen Oxides				
Sulfur Oxides		.00121		
Hydrogen Sulfide				
Water				
			C_1^+ HC .00153	C_2^+ HC .00108
Sample Tap Location		Incinerator Feed	None	None
Date or Frequency of Sampling	1968	2 or 3 times/10 Yr.		
Type of Analysis	GLC	GLC, Orsat, Wet		
Odor Problem	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow - SCFM Per Stack	1,000	24,000		
Number	1	1	1	1
Height - Feet	200	120	160	210
Diameter - Inches	24	36	10	10
Exit Gas Temperatures - F°	200	780	200	200
Emission Control Devices	No	Yes	No	No
Type - Flare				
Water Scrubber				
Refrigerated Condenser & K. O. Drum				
Other		X Incinerator		
Catalog I. D. Number		EL - 9		
Total Hydrocarbon Emissions - Ton/Ton Ethylene $^{(g)}$	.00108			
Total Particulate & Aerosol Emissions Ton/Tone Ethylene				
Total NO_x				
Total SO_x	.00121			
Total CO				

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company					
Location					
EPA Code Number		11-11			
Date on-stream					
Capacity - Tons of Ethylene/Yr.		197,500			
Average Production - Ethylene Tons/Yr.					
Range in Production - % of Max. (f)		0			
Emissions to Atmosphere					
Stream	Flare Stack	Safety Valve Discharge Stack	Gas Turbine Lube Oil Vent	Compressor Oil Reservoir Vent	Compressor Sour Drum K. O. Vent
Flow - Lbs./Hr.	Unspecified (Variable)	Unspecified	225	78	80
Flow Characteristic - Continuous or Intermittent	Continuous	Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow		Unspecified			
Composition - Tons/Ton of Ethylene					
Hydrogen		} 0.00006 (j)			
Methane			< 0.000002	< 0.000001	0.00016
Ethane		} 0.0005 (j)	< 0.000001	< 0.000004	0.001
Ethylene					
Propane		} 0.0011 (j)	0.00013	< 0.000005	0.0005
Propylene					
C_4 + Hydrocarbons		) 0.00008 (j)	< 0.000002	< 0.00002	Trace
Acetylene					
Oxygen	+		} 0.005	} 0.0017	} 0.00013
Nitrogen	+				
Carbon Monoxide					
Carbon Dioxide	+				
Nitrogen Oxides					
Sulfur Oxides					
Hydrogen Sulfide					
Water	+				
Sample Tap Location	None	Not Specified	Not Specified (Simple)	Not Specified (Simple)	Not Specified (Simple)
Date or Frequency of Sampling		Not Specified	Once	Once	Once
Type of Analysis		Not Specified	Mass Spectronmeter	Mass Spectrometer	Mass Spectrograph
Odor Problem	None	None	None	None	No
Vent Stacks					
Flow, SCFM Per Stack	Unspecified	Unspecified	49	17	17
Number	1	1	1	1	1
Height - Feet	300	150	50	60	60
Diameter - Inches	36	20	2	4	4
Exit Gas Temperatures - F°	Unspecified	Unspecified	80	80	80
Emission Control Devices	Yes	None	None	None	None
Type - Flare	X				
Water Scrubber					
Refrigerated Condenser & K. O. Drum					
Other					
Catalog I. D. Number	EL-33				
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)		See Continuation			
Total Particulate & Aerosol Emissions Ton/Ton Ethylene					
Total NO_x					
Total SO_x					
Total CO					

TABLE EI-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

Company			
Location			
EPA Code Number	11-11		
Date on-stream			
Capacity - Tons of Ethylene/Yr.	197,500		
Average Production - Ethylene Tons/Yr.			
Range in Production - % of Max. (f)	0		
Emissions to Atmosphere			
Stream	Sour Seal Oil Vent	Analyzer Vent	Fourth Stage Relief Valve Vent
Flow - Lbs./Hr.	150	< 0.01	245 000
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Intermittent
if Intermittent - Hrs./Yr. Flow			0.25 (i)
Composition - Tons/Ton of Ethylene			
Hydrogen			
Methane	0.0003	$<10^{-6}$	
Ethane		$<10^{-6}$	10^{-6}
Ethylene	0.00074		10^{-6}
Propane	0.00148	$<10^{-6}$	
Propylene			0.000155
C_4 + Hydrocarbons	0.00053		
Acetylene			
Oxygen	0.00028		
Nitrogen			
Carbon Monoxide			
Carbon Dioxide			
Nitrogen Oxides			
Sulfur Oxides			
Hydrogen Sulfide			
Water			
Sample Tap Location	Not Specified (Simple)	Not Specified (Simple)	Not Specified (Simple)
Date or Frequency of Sampling	Once	Not Specified	Not Specified
Type of Analysis	Mass Spectrograph	Mass Spectrograph	Mass Spectrometer
Odor Problem	No	No	No
Vent Stacks			
Flow, SCFM Per Stack	26	0.1 SCFH	35,000
Number	1	1	
Height - Feet	50	10	
Diameter - Inches	1	1/4	
Exit Gas Temperatures - F°	80	80	< 196
Emission Control Devices			
Type - Flare	None	None	None
Water Scrubber			
Refrigerated Condenser & K. O. Drum			
Other			
Catalog I. D. Number			
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)		See Continuation	
Total Particulate & Aerosol Emissions Ton/Ton Ethylene			
Total NO_x			
Total SO_x			
Total CO			

TABLE EI-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company				
Location				
EPA Code Number	11-11			
Date on-stream				
Capacity - Tons of Ethylene/Yr	197,500			
Average Production - Ethylene Tons/Yr.				
Range in Production - % of Max. (f)	0			
Emissions to Atmosphere				
Stream	Depropanizer Relief Valve Vent (Bottom)	Depropanizer Relief Valve Vent (Top)	Depropanizer Overhead Relief Vent	Debutanizer Overhead Relief Vent
Flow - Lbs./Hr.	214,000	230,000	230,000	36,000
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Intermittent	Intermittent
if Intermittent - Hrs./Yr. Flow	0.25 (i)	0.5 (i)	0.25 (i)	0.25 (i)
Composition - Tons/Ton of Ethylene				
Hydrogen Methane	} 0.00003	} 0.00003	} 0.000015	
Ethane Ethylene	} 0.000053	} 0.00013	} 0.000065	
Propane Propylene	} 0.000035	} 0.00014	} 0.00007	} $<10^{-6}$
C_4 + Hydrocarbons	0.000018	$<10^{-6}$	$<10^{-6}$	0.000023
Acetylene				
Oxygen				
Nitrogen				
Carbon Monoxide				
Carbon Dioxide				
Nitrogen Oxides				
Sulfur Oxides				
Hydrogen Sulfide				
Water				
Sample Tap Location	Not Specified (Simple)	Not Specified (Simple)	Not Specified (Simple)	Not Specified (Simple)
Date or Frequency of Sampling	Not Specified	Not Specified	Not Specified	Twice Weekly
Type of Analysis	Mass Spectrometer	Mass Spectrometer	Mass Spectrometer	Gas Chromatograph
Odor Problem	No	No	No	No
Vent Stacks	None	None	None	None
Flow, SCFM Per Stack	46,000	46,000	45,300	3,900
Number				
Height - Feet				
Diameter - Inches				
Exit Gas Temperatures - F°	<40	≤ -5	≤ 50	<115
Emission Control Devices	None	None	None	None
Type - Flare				
Water Scrubber				
Refrigerated Condenser & K. O. Drum				
Other				
Catalog I. D. Number				
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)	See Continuation			
Total Particulate & Aerosol Emissions Ton/Ton Ethylene				
Total NO_x				
Total SO_x				
Total CO				

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company			
Location			
EPA Code Number	11-11		
Date on-stream			
Capacity - Tons of Ethylene/Yr.	197,500		
Average Production - Ethylene Tons/Yr.			
Range in Production - % of Max. (f)	0		
Emissions to Atmosphere			
Stream	Remote Operated Valve Vent	Lube Oil Reservoir Vent	Seal Oil Reservoir Vent
Flow - Lbs./Hr.	320	6,100	40
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow			
Composition - Tons/Ton of Ethylene			
Hydrogen			
Methane	0.006	0.001	<0.00001
Ethane	0.0004	>0.00001	<0.00001
Ethylene			
Propane	0.00013	<0.00001	<0.00001
Propylene			
C_4 + Hydrocarbons	0.00014	0.0001	<0.00001
Acetylene			
Oxygen	}0.00045	}0.134	}<0.001
Nitrogen			
Carbon Monoxide			
Carbon Dioxide			
Nitrogen Oxides			
Sulfur Oxides			
Hydrogen Sulfide			
Water			
Sample Tap Location	Not Specified (Simple)	Not Specified (Simple)	Not Specified (Simple)
Date or Frequency of Sampling	Once	Once	Once
Type of Analysis	Mass Spectrograph	Mass Spectrograph	Mass Spectrograph
Odor Problem	No	No	No
Vent Stacks			
Flow, SCFM Per Stack	115	1,320	8
Number	1	1	1
Height - Feet	50	50	8
Diameter - Inches	6	6	3
Exit Gas Temperatures - F°	80	80	80
Emission Control Devices	None	None	None
Type - Flare			
Water Scrubber			
Refrigerated Condenser & K. O. Drum			
Other			
Catalog I. D. Number			
Total Hydrocarbon Emissions - Tons/Ton Ethylene (g)		0.00753	
Total Particulate & Aerosol Emissions Ton/Ton Ethylene		None	
Total NO_x		None	
Total SO_x		None	
Total CO		None	

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company			
Location			
EPA Code Number	11-12		11-3
Date on-stream			
Capacity - Tons of Ethylene/Yr.	225,000		800,000
Average Production - Ethylene Tons/Yr.	225,000		
Range in Production - % of Max. (f)	0		
Emissions to Atmosphere			
Stream	Emergency Vent	Emergency Vent	(e) Not Specified
	Prod. Fract.	Prod. Fract.	
Flow - Lbs./Hr.	50,000 (Max.)	50,000 (Max.)	
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	
if Intermittent - Hrs./Yr. Flow	Not Specified	Not Specified	
Composition - Tons/Ton of Ethylene			
Hydrogen			
Methane			
Ethane			
Ethene			
Propane			
Propene			
C_4^+ Hydrocarbons			
Acetylene			
Oxygen			
Nitrogen			
Carbon Monoxide			
Carbon Dioxide			
Nitrogen Oxides			
Sulfur Oxides			
Hydrogen Sulfide			
Water			
Sample Tap Location			
Date or Frequency of Sampling	Weekly	Weekly	
Type of Analysis	GLC	GLC	
Odor Problem	No	No	
Vent Stacks	Yes	Yes	
Flow - SCFM per Stack	Not Specified	Not Specified	
Number	1	1	
Height - Feet	Ground Level	Ground Level	
Diameter - Inches			
Exit Gas Temperatures - °F			
Emission Control Devices	Yes	Yes	
Type - Flare	X	X	
Water Scrubber			
Refrigerated Condenser & K. O. Drum			
Other	X Smoke Suppressor	X Smoke Suppressor	
Catalog I. D. Number	EL - 24	EL - 24	
Total Hydrocarbon Emissions - Ton/Ton Ethylene (g)	Not Specified		
Total Particulate & Aerosol Emissions Ton/Ton Ethylene			
Total NO_x			
Total SO_x			
Total CO			

TABLE EL-III
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

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Company				
Location				
EPA Code Number	11-13			
Date on-stream				
Capacity - Tons of Ethylene/Yr.	300,000			
Range in Production - % of Max. (f)				
Emissions to Atmosphere				
Stream	Vent From Furnace Decoking	Acetylene Converter Regeneration Vent	Caustic Neutraliz. Vent	Plant Flare System
Flow - lbs./Hr.		460	20,672	910 (a)
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Continuous	Continuous (After Burning)
If Intermittent - Hrs./Yr. Flow		408		
Composition - Tons/Ton of Ethylene				
Hydrogen				
Methane				
Ethane				
Ethene				
Propane				
Propene				
C_4^+ Hydrocarbons				
Acetylene				
Oxygen		Not Specified	.06693	
Nitrogen		Not Specified	.22406	
Carbon Monoxide	Not Specified	Not Specified		
Carbon Dioxide	Not Specified	Not Specified		.03486
Nitrogen Oxides				
Sulfur Oxides				
Hydrogen Sulfide			.00017	
Water	.02400 Coke .00001	Not Specified		.02852
Sample Tap Location	@ Furnace	Not Sampled	Not Sampled	Not Sampled
Date or Frequency of Sampling	1969			
Type of Analysis	Coulter Counter		Engr. Est.	Calcuated
Odor Problem	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow - SCFM Per Stack	4,290		4,500	
Number	1	1	1	1
Height - Feet	78.5	42	93	130
Diameter - Inches	14	8	8	36
Exit Gas Temperatures - F°	212	140	Ambient	1800 - 2500
Emission Control Devices	Yes	Yes	Yes	Yes
Type - Flare				X
Water Scrubber	X			
Refrigerated Condenser & E. O. Drum		X		
Other			X Vapor Collectors & Dilution Device	
Catalog I. D. Number	EL - 10	EL - 15	EL - 11	EL - 30
Total Hydrocarbon **Emissions** - Ton/Ton Ethylene (e)				
Total Particulate & Aerosol Emissions - Ton/Ton Ethylene				
Total NOx				
Total SO_x				
Total CO				

TABLE EL-III

EXPLANATION OF FOOTNOTES
NATIONAL EMISSIONS INVENTORY
ETHYLENE PRODUCTION

(a) The flow rate given describes the stream prior to combustion.

(b) 80,000 lb./hr. of a 92% methane stream - most probably the demethanizer overhead - is used to supplement the fuel to the pyrolysis furnace. This stream and it's resultant atmospheric emissions (CO_2 & H_2O) are not detailed elsewhere in this report.

(c) This stream is not emitted to the atmosphere, it is sent to a Claus plant.

(d) Boiler stack used.

(e) Although there is a wealth of information in this report; quantitative data on emissions are conspicuous by their absence. (with exception of motor exhaust data)

(f) Difference between maximum and minimum quarterly production divided by maximum quarterly production.

(g) Includes H_2S. Excludes CH_4 & H_2.

(h) Three identical scrubbers are provided on the acetylene converter, propadiene converter and hydrogenation catalyst regeneration vents. The emissions from each are essentially the same.

(i) Estimated maximum per year.

(j) Calculated on basis of total of maximum estimated releases from each relief valve in circuit.

TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF ETHYLENE VIA THE PYROLYSIS OF LIGHT HYDROCARBONS

Page 1 of 8

	CRACKING FURNACE		
WATER SCRUBBERS - Flow Diagram Stream I. D.	(A)	(A)	(A)
Device I. D. Number	EL - 1	EL - 2 (1)	EL - 10
EPA Code No. for plant using	11-9	11-3	11-13
Purpose - Control Emissions of	Coke Particles	Coke Particles	Coke Particles
Type - **Spray**		X	
Packed Column		X	
Trays - Type		Seive	
Number		5	
Plenum Chamber	X		X
Other			w/Venturi Mixer
Water Rate - GPM	Not Known	Not Specified	120
Design Temp. (operating temp.) °F	(560)	450	(212)
Gas Rate - SCFM (lb./hr.)	Approx. (45,000)	(2,600)	12,000
T-T Height - Ft.	18	19	9.2
Diameter - Ft.	12	4	4
Washed Gases to Stack	Via-Device EL - 12	Yes	Yes
Stack Height - Ft.	260	25	78.5
Stack Diameter - Ft.	16	.3	1.2
Installed Cost - Material & Labor, $	100,000	(Total) 870,000	105,000
Installed Cost - ¢/lb. of Ethylene	.0083	(Total) .0544	.0175
Operating Cost - Annual, $	6,000	(Total) 5,800	< 1,000
Operating Cost - ¢/lb. of Ethylene	Not Specified	Not Specified	< .0002
Efficiency (IX)			98% (Particulates)

TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF ETHYLENE VIA THE PYROLYSIS OF LIGHT HYDROCARBONS

Page 2 of 8

	Quench Section	"Acid Gas" Removal Section
INCINERATION DEVICES - Flow Diagram Stream I. D.	(B)	(C)
Device I.D. Number	EL-3 (II)	EL-9
EPA Code No. for plant using	11-3	11-10
Types of Compounds Incinerated	Gas ex. H_2O Drum	"Waste" Gas
Type Device - Flare	X	
Incinerator		X
Other		
Materials Incinerated SCFM (lbs./hr.)	Not Specified	
Auxiliary Fuel Req'd. - Excluding Pilots	No	Yes
Auxiliary Fuel Type		Gas
Auxiliary Fuel Rate - BTU/hr.		Not Specified
Device or Stack Height - Ft.	38	120
Installed Cost - Material & Labor - $	(Total) 28,000	26,200
Installed Cost - ¢/lb. of Ethylene/Yr.	(Total) .0018	.0040
Operating Cost - Annual - $	(Total) 500	9,200
Operating Cost - ¢/lb. of Ethylene	(Total) <.0001	.0014
Efficiency - CCR - % - (X)	~100	~100
Efficiency - SERR - % - (X)	< 100	<100

TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES
CURRENTLY USED IN THE PRODUCTION OF
ETHYLENE
VIA THE
PYROLYSIS OF LIGHT HYDROCARBONS

Page 3 of 8

	"Acid Gas" Removal Section					
K. O. DRUMS - Flow Diagram Stream I. D.	(C)	(D)	(C)	(C)	(D)	
Device I. D. Number	EL - 4	EL - 5	EL - 6	EL - 7	EL - 8	EL - 11
EPA Code No. for plant using	11-8	11-8	11-5	11-5	11-5	11-13
Purpose - Control Emission of	Wash H_2O Off-gas	Caustic Soln. Off-gas	Wash H_2O Off-gas	Wash H_2O Off-gas	Caustic Soln. Off-gas	Waste Liquor Off-gas
Type - Condenser & K. O. Drum						
Demister						
Degasser	X	X	X	X	X	
Other						X (III)
Design Press. (operating press) PSIG	(15)	(62)	(10)	(-5)	(10)	Atmos.
Design Temp. (operating temp.) - F°	(100)	(100)	(10)	(110)	(110)	Not Specified
Feed Rate of Stream Treated						
Liquid - lb./hr. (GPM)	X (12)	X (16)	X (10)	X (10)	X (20)	
Gas - lb./hr. SCFM)						X
T-T Height (length) - Ft.	6	6	(17)	8	10	(sump) 12
Diameter - Ft.	2	2	4.5	3	4	(sump) 3.5
Vent Gases to Stack	Return to process	Return to process	Return to process	Return to process	Return to process	Yes
Stack Height - Ft.						93
Stack Diameter - Ft.						.7
SCFM/Stack						Not Specified
Installed Cost - Material & Labor - $	1,000	1,000	8,535		3,900	29,000
Installed Cost - ¢/lb. of Ethylene - Yr.	.0004	.0004	.0009		.0004	.0048
Operating Cost - Annual - $	Not Specified	Not Specified	Not Specified		Not Specified	Not Specified
Operating Cost - ¢/lb. of Ethylene	"	"	"	"	"	"
Efficiency (IX)	"	"	"	"	"	"

TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES

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ACETYLENE
CONVERSION SECTION

WATER SCRUBBERS - Flow Diagram Stream I. D.	(e)	(e)	(e)
Device I.D. Number	EL-13	EL-14 (V)	EL-16 (VI)
EPA Code No. for plant using	11-8	11-5	11-3
Purpose - Control Emission of	Regeneration Gas	Regeneration Gas	Regeneration Gas
Type - Spray	X (Multi-level)	X	X
Packed Column			
Trays - Type			
Number			
Plenum Chamber	X	X	X
Other			
Water Rate - GPM	250	(Total) - 1500	Not Specified
Design Temp. (operating temp.) - F°	Not Specified	140	
GAS Rate - SCRM (lbs./hr.)	Not Specified	Not Specified	
T-T Height - Ft.	20	6	4
Diameter - Ft.	1.3	4	2
Washed Gases to Stack	Yes	Yes	Yes
Stack Height - Ft.	175	30	31
Stack Diameter - Ft.	.5	1	1
Installed Cost - Material & Labor, $	5,000	(Total) 10,000	(Total) 5,000
Installed Cost - ¢/lb. of Ethylene - Yr.	.0020	(Total) .0011	(Total) .0003
Operating Cost - Annual - $	Not Specified	Not Specified	(Total) 300
Operating Cost - ¢/lb. of Ethylene	"	"	(Total) >.0001
Efficiency (IX)	"	"	Not Specified

K. O. DRUMS - Flow Diagram Stream I. D.	(e)	(e)
Device I. D. Number	EL-12	EL-15
EPA Code No. for plant using	11-9	11-13
Purpose - Control Emission of	Regeneration Gas	Regeneration Gas
Type - Condenser & K. O. Drum		X
Demister	X	
Degasser		
Other		
Design Press. (operating press.) PSIG	(Atmos.)	(Atmos.)
Design Temp. (operating temp.) F°	Not Specified	(140)
Feed Rate of stream treated	Not Specified	Not Specified
Liquid - lbs./hr. (GPM)		
Gas - lbs./hr. (GPM)		
T-T Height (length) - ft.	23.5	6
Diameter - ft.	13	2
Vent Gases to Stack	Yes (IV)	Yes
Stack Height - ft.	260	42
Stack Diameter - ft.	16	.7
SCFM/Stack	300,000	
Installed Cost - Material & Labor - $	350,000	28,000
Installed Cost - ¢/lb. of Ethylene - Yr.	.0292	.0047
Operating Cost - Annual - $	6,000	Not Specified
Operating Costs - ¢/lb. of ethylene	.0005	"
Efficiency (IX)	Not Specified	"

TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES

Page 5 of 8

FRACTIONATION SECTION (INCLUDING MAIN PLANT BLOWDOWN & FLARE SYSTEM)

INCINERATION DEVICES							
Device I. D. Number	EL - 17	EL - 18	EL - 19	EL - 20	EL - 21	EL - 22	EL - 23
EPA Code No. for plant using	11-9	11-2	11-5	11-7	11-8	11-1	11-4 (VII)
Types of Compounds Incinerated	All Emergency Vents	Acid Gas & All Emergency Vents	All Emergency Vents	All Waste Gases & Emergency Vents	All Emergency Vents	All Waste Gases & Emergency Vents	All Emergency Vents
Type Device - Flare	X	X	X	X	X	X	X
Incinerator							
Other							
Materials Incinerated SCFM (lb./hr.)	Not Specified	Not Specified	(170,000) Max.	1500	(50,000) Max.	430 (Normal)	Not Specified
Auxilliary Fuel Req'd - Excluding Pilot	No			No	No	No	No
Auxilliary Fuel Type							
Auxilliary Fuel Rate - BTU/hr.							
Device Elevation - Ft. above grade	360	120	265	225	200	240	Not Specified but Horizontal
Installed Cost - Material & Labor, $	2,934,000	500,000	518,700	45,000	78,600	663,000	(Total) 73,000
Installed Cost - ¢/lb. of Ethylene - Yr.	.2445	.0649	.0576	.0069	.0308	.0553	(Total) .0252
Operating Cost - Annual	199,800	50,000	Not Specified	20,000	5,500	53,500	(Total) 1,400
Operating Cost - ¢/lb. of Ethylene	.0167	.0065		.0031	.0022	.0045	(Total) .0005
Efficiency - CCR - % (X)	100%	100	~100	~100	~100	~100	~100
Efficiency - SERR - % (X)	100	53	<100	< 100	< 100	< 100	< 100

INCINERATION DEVICES							
Device I. D. Number	EL - 24	EL - 25	EL - 26	EL - 27	EL - 28	EL - 29	EL - 30
EPA Code No. for plant using	11-12 (VII)	11-10	11-10	11-3 (VIII)	11-3 (VIII)	11-3 (VIII)	11-13
Types of Compounds Incinerated	All Emergency Vents	Emergency Vent	Emergency Vent	Purge Gas Vents and Blowdown	Purge Gas Vents and Blowdown	Purge Gas Vents and Blowdown	Emergency Vent
Type Device - Flare	X	X	X	X	X	X	X
Incinerator							
Other							
Materials Incinerated SCFM (lb./hr.)	Total (100,000) Max.	(1,000,000) Max.	(100,000) Max.	Not Specified	Not Specified	Total (560,000) Max.	(160,000) Max.
Auxilliary Fuel Req'd - Excluding Pilot	No						
Auxilliary Fuel Type							
Auxilliary Fuel Rate BTU/Hr.							
Device Elevation - Ft. above grade	Not Specified but Horizontal	200	150	150	150	150	130
Installed Cost - Material & Labor, $	(Total) 81,000	329,000	85,000	(Total) 275,000	(Total) 150,000	(Total) 500,000	Not Specified
Installed Cost - ¢/lb. of Ethylene - Yr.	(Total) .0180	.0498	.0129	(Total) .0172	(Total) .0094	(Total) .0313	
Operating Cost - Annual	(Total) 10,000	142,000		(Total) 10,000	(Total) 10,000	(Total) 10,000	
Operating Cost - ¢/lb. of Ethylene	(Total) .0022	.0215		(Total) .0006	(Total) .0006	(Total) .0006	
Efficiency - CCR - % (X)	~100	~100	~100	~100	~100	~100	~100
Efficiency - SERR - % (X)	< 100	< 100	< 100	< 100	< 100	< 100	< 100

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TABLE EL-IV
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF
ETHYLENE
VIA THE
PYROLYSIS OF LIGHT HYDROCARBONS

ACETYLENE CONVERSION SECTION

WATER SCRUBBERS - Flow Diagram Stream I. D.	
Device I. D. Number	EL-31 (3 units)
EPA Code No. for plant using	11-6
Purpose - Control Emissions of	Regeneration gas
Type - Spray	x
Packed Column	
Trays - Type	
Number	
Plenum Chamber	
Other	
Water Rate - GPM	0.75 (?)
Design Temp. (operating temp.) F°	212° F
Gas Rate - SCFM (lb./hr.)	steam 10,000 - air 900
T-T Height - Ft.	4.5
Diameter - In.	30 IPS
Washed Gases to Stack	Yes (3 stacks)
Stack Height - Ft.	12
Stack Diameter - Ft.	6
Installed Cost - Material & Labor, $	7,050 (total for all three)
Installed Cost - ¢/lb. of Ethylene	0.0035
Operating Cost - Annual, $	4,200
Operating Cost - ¢/lb. of Ethylene	0.0021
Efficiency (IX)	100

TABLE EL-IV

CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF ETHYLENE VIA THE PYROLYSIS OF LIGHT HYDROCARBONS

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MAIN PLANT FLARE SYSTEM

INCINERATION DEVICES - Flow Diagram Stream I.D.		
Device I. D. Number	EL-32	EL-33
EPA Code No. **for plant** using	11-6	11-11
Types of Compounds Incinerated	Hydrocarbons	Hydrocarbons
Type Device - Flare	+	+
Incinerator		
Other		
Materials Incinerated SCFM (lb./hr.)	Unspecified	Unspecified
Auxilliary Fuel Req'd. - Excluding Pilots	No	No
Auxilliary Fuel Type		
Auxilliary Fuel Rate - BTU/hr.		
Device or Stack Height - Ft.	Unspecified	300
Installed Cost - Material & Labor, $	Unspecified	310,000
Installed Cost - ¢/lb. of Ethylene/Yr.		0.0785
Operating Cost - Annual - $	Unspecified	52,450
Operating Cost - ¢/lb. of Ethylene		0.0133
Efficiency - CER - % (X)	100	100
Efficiency - SERR - % (X)	<100	<100

TABLE EL-IV
EXPLANATION OF NOTES
CATALOG OF EMISSION CONTROL DEVICES CURRENTLY USED IN THE PRODUCTION OF ETHYLENE VIA THE PYROLYSIS OF LIGHT HYDROCARBONS

Page 8 of 8

I There are fifty-eight (58) decoking scrubbers in plant # 11-3. One for each furnace.

II There are five (5) waste gas flares in plant # 11-3.

III Device EL - 11 accomplishes the following:
  (1) Strips dissolved gases from spent caustic and vents them to atmosphere.
  (2) Gather fumes from neutralization pit and vents them at elevation.

IV Utilizing boiler stack.

V Device consists of two paralled drums, used simultaneously.

VI There are three regenerating gas scrubbers.

VII There are two identical horizontal flare systems.

VIII There are two similar flares.

IX Defined as percent removal of total air pollutants in stream being treated.

X See Appendix V for definitions.

TABLE EL-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980*	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
22,295	2,800	19,495	40,000	40,000	20,505	1,000	20-21

Note: All capacities in mm lbs./year.

*1980 demand based on study prepared for EPA by Process Research, Inc. and C. E. P. Vol. 68, No. 9.

TABLE EL-VI
SUMMARY OF EMISSION SOURCES (1)

Pollutant	Source Furnace Decoking	Quench Tower	Acid Gas Removal	Compressors	Distillation Train	Fugitive Emissions	Total
Hydrocarbons		.00001	.00001	.00010	.00050	.00010	.00072
Particulates	.00001						.00001
NO_x					.00001		.00001
SO_x			.00300 (2)				.00300
CO		.00001					.00001

Note

(1) Pollutant concentrations in lb./lb. of ethylene.

(2) Adjusted for predicted trend in feedstock.

TABLE EL-VII
WEIGHTED EMISSIONS RATES

Chemical Ethylene

Process Pyrolysis

Increased Capacity 20.5 billion lbs./yr.

Pollutant	Emissions, lbs./lb.	Increased Emissions MM lbs./year	Weighting Factors	Weighted Emissions MM lbs./year
Hydrocarbons	.00072	14.8	80	1180.8
Particulates	.00001	.2	60	12.0
NO_x	.00001	.2	40	8.0
SO_x	.003 (a)	61.5	20	1230.3
CO	.00001	.2	1	.2

Significant Emission Index = 2431.3 (MM lbs./yr.)

(a) Adjusted for predicted trend in feedstock.

Ethylene Dichloride (Direct)

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II.	Process Description	EDC-2
III.	Plant Emissions	EDC-3
IV.	Emission Control	EDC-5
V.	Significance of Producers	EDC-7
VI.	Ethylene Dichloride Producers	EDC-8

List of Illustrations and Tables

Flow Diagram	Figure EDC-I
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Gross Heat Balance	Table EDC-II
Emission Inventory	Table EDC-III
Catalog of Emission Control Devices	Table EDC-IV
Number of New Plants by 1980	Table EDC-V
Emission Source Summary	Table EDC-VI
Weighted Emission Rates	Table EDC-VII

I. Introduction

Ethylene dichloride (1, 2 dichloroethane) was the earliest known chlorinated hydrocarbon, having been produced by four Dutchmen in 1795. At ordinary temperatures it is an oily, colorless liquid with an odor resembling that of chloroform. The vapor has an irritant effect on the respiratory tract and is toxic.

Primarily, ethylene dichloride (EDC) is used to produce vinyl chloride monomer by dehydrohalogenation. Over 80% of the ethylene dichloride manufactured goes to this purpose. Virtually all EDC producers have vinyl chloride plants nearby. Other uses for EDC are in solvent manufacture, ethyleneamine production and as a lead scavenger in antiknock fluids.

Two commercial processes account for most of the ethylene dichloride produced today. One is the direct chlorination of ethylene with chlorine. The other is an oxychlorination process in which ethylene, hydrogen chloride and oxygen react to form the same product. Presently almost all production centers around large plants employing a balanced combination of these two processes. These balanced plants use the hydrogen chloride recovered when ethylene dichloride is dehydrohalogenated as feed to the oxychlorination reactor. This requires about a 50/50 split between direct chlorination and oxychlorination for a completely balanced operation.

Total ethylene dichloride capacity presently is 9.6 billion lbs./year, about 58% of the total is direct chlorination, and about 42% by oxychlorination. Capacity is expected to rise by 12.5 billion lbs./year between now and 1980 requiring around 9 - 10 large balanced operations.

This report directs its attention to the direct chlorination process. The major source of air emissions from this process is the hydrogen chloride scrubber vent. Quantities of chlorinated hydrocarbons and light hydrocarbons are emitted to the atmosphere from this source. In general, air emissions from ethylene dichloride production by direct chlorination can be best described as moderate.

An intensive review of air pollution from the oxychlorination process is provided in an in-depth study of that process, as reported in Report No. EPA-450/3-73-006.

II. Process Description

In the direct chlorination process, ethylene dichloride is produced by the chemical combination of ethylene and chloride.

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4 Cl_2$$

(See Figure EDC 1)

Chlorine and a substantially stoichiometric amount of ethylene are fed into a reactor under constant temperature conditons, excesses of either reactant result in raw material losses. The reaction usually takes place in the liquid phase with a considerable excess of reaction product, although depending upon design, excess reaction product may not be necessary. The exothermic heat of reaction, 52 kcal./mole, is removed by jacketed walls, internal cooling coils or external heat exchange. When considerable amounts of inert gases are present in the feed, some packing might be necessary to improve liquid-gas contact. Typical reaction conditions are temperatures of 100-120° F and pressures in the range of 10-20 PSIG. Overall process yield of ethylene dichloride from chlorine is generally better than 98 percent if high purity reactants are used. However, the present of impurities in either ethylene or chlorine will reduce the reaction yield. Usually a liquid and a vapor stream exit from the reactor. The vapors pass through water cooled condensers, and in some cases refrigerated exchangers where some ethylene dichloride is recovered. The vapors are sent through an absorbing column where dichloride is recovered. The vapors are sent through an absorbing column where small quantities of hydrogen chloride and chlorine are removed. The scrubbing liquid is either water or dilute caustic, depending on the amount of chlorine that is desired to be removed.

The crude liquid ethylene dichloride that exists from the reactor must be refined for commercial use. Frequently, in a balanced direct chlorination-oxychlorination plant, the crude ethylene dichloride from both processes are combined and refined together. In any case, the refining steps are similar. The crude is washed with a dilute caustic solution. Greater than 10 percent caustic is never used because it might cause product decomposition. Water is removed either by coalescing and phase separation or by phase separation and light ends distillation. The purity of the crude (amount of light hydrocarbons present) and the desired purity of the product dictate equipment design. Heavy ends, useful chlorinated hydrocarbons and tars are removed in a distillation column and product passes overhead. In some plants, final product distillation is not provided since crude ethylene dichloride purity (98+%) is adequate for many applications.

An overall material balance and an energy balance around the reactor section are provided in Tables I and II respectively.

III. Plant Emissions

A. Continuous Air Emissions

1. Scrubber Vent

The major source of air emissions from the direct chlorination of ethylene, are gases, mainly inerts, vented from the scrubbing column. The stream contains small amounts of ethylene, ethylene dichloride, vinyl chloride, ethylchloride as well as inert impurities in the feed. Small quantities of hydrogen chloride and chlorine may be emitted depending on the scrubbing medium (caustic or water) and the unit's capacity. Most plants employ condensers to recover some ethylene dichloride before the stream enters the scrubber. The efficiency of recovery, of course, depends on the final gas temperature. One plant which cools the gases and vapors to -10° F prior to scrubbing showed significantly lower emissions than the other two respondents. Unfortunately, since the inlet to the scrubber consisted of a combined stream from oxychlorination and direct chlorination the data may not be typical for a plant providing ethylene dichloride by direct chlorination only.

2. Product Storage Losses

Ethylene dichloride storage tanks usually have simple vents to the atmosphere because the vapor pressure (three PSI @ 100° F) is low. In some cases, nitrogen pading is used to help minimize emissions. It is estimated that EDC losses due to product storage equal about 0.0006 lbs./lb. EDC.

3. Decanter Vents

Small amounts of EDC are released to the atmosphere during washing in plant 12-1. In the future, it was reported that the vapors will be recovered by chilling.

B. Intermittent Air Emissions

No sources of intermittent air emissions were reported.

C. Liquid Wastes

Waste water is produced from the scrubbing of vented gases and the caustic washing of crude EDC. Only plant 12-1 provides an estimate of waste water flow. It reported 1,000 GPM of waste water due primarily to indirect cooling.

D. Solid Waste

Tars produced in the heavy ends column are usually disposed of by land fill or by incineration. If a catalyst is used, it too is trucked to a disposal site. Respondent 21-2 reports .00027 lbs./lb. EDC of tar and catalyst sent to sanitary land fill.

E. Odor

Reports on the production of ethylene dichloride by direct chlorination indicate that the process does not present an odor problem. No complaints were reported by the respondents although odors of EDC and chlorine are detectable on-site.

F. Fugitive Emissions

Fugitive emissions due to leaks, spills and miscellaneous causes are believed to be between .0007 and .00007 lbs./lb. EDC.

IV. Emission Control

The emission control devices that have been reported as being employed by direct chlorination EDC producers are summarily described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been made available. Two types of efficiencies have been calculated.

1) "SE" - Specific Efficiency

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

2) "SERR" - Significance of Emission Reduction Rating

$$SERR = \frac{\Sigma(\text{pollutant} \times \text{weighting factor})\text{in} - \Sigma(\text{pollutant} \times \text{weighting factor*})\text{out}}{\Sigma(\text{pollutant} \times \text{weighting factor})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

A brief description of the emission control devices employed follows:

Scrubbers

A scrubber is usually employed to remove small amounts of HCl and in some cases chlorine left in the non-condensed reactor effluent. Both water and caustic scrubbers are used in U. S. plants. The water variety are able to remove most if not all of the HCl, but dilute caustic is generally necessary to eliminate all the chlorine from the vent gas. Some EDC may also be absorbed depending on the operating conditions. Below is a brief summary of the efficiencies of some of the devices reported.

Plant	Device I. D. No.	"SE" - HCl	"SE" - Cl_2	"SERR"
12-1	SC-I	100%	100%	25%
31-1	SC-IV	75%	Small	18%

Condensers

Although condensers of some sort for the gaseous reactor effluent stream are reported by all respondents only plant 31-1 cools the stream down low enough (-10° F) to recover most of the EDC present. The "SE" for removal of EDC for this device is 97.9%. Since the respondent reports a net credit of $45,000/year as operating expenses on an initial investment of $125,000, it would seem that this type of device would be a worthwhile investment for future plants.

General Comments and Future Plans

Recommendations

Since most future plants are expected to employ a balanced process and undesirable components of the emissions from the direct chlorination scrubber vent are similar to those in the vent from the oxychlorination scrubber, combining the two streams for further treatment seems to be practical, economic and expedient. This is a scheme which has already been demonstrated, so no development program will be required.

Future Plans for Plants Participating in the Survey

Respondent 12-1 reports that plans are under way to compress the scrubber vent discharge and use it as feed to an existing unit.

Respondent 12-2 will have an incinerator on line for the scrubber vent gases before the end of 1973.

V. Significance of Pollution

It is recommended that no in-depth study of this process be considered at this time. The quantity of air pollutants released to the atmosphere are considerably lower for the direct chlorination process than for the oxy-chlorination process and are lower than several processes currently under in-depth study.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

On a weighted emissions basis a Significant Emissions Index ov 2,738 has been calculated in Table VII. This is substantially lower than the SEI's of some other processes under in-depth study. Hence, the recommendation to exclude an in-depth study of ethylene dichloride by direct chlorination from the in-depth scope of the work for this project.

VI. Ethylene Dichloride Producers

Company	Location	Capacity, MM Lbs./Yr.	Direct Chlorination	Oxychlorination
Allied Chemical Corporation	Baton Rouge, La.	645	430	215
American Chemical Company	Long Beach, Calif.	325	225	100
Conoco Chemicals	Lake Charles, La.	968	476	492
Diamond Shamrock Chemical Co.	Deer Park, Texas	265	95	170
Dow Chemical Company	Freeport, Texas	1,100	628	472
Dow Chemical Company	Plaquemine, La.	1,160*	600	560
Ethyl Corporation	Baton Rouge, La.	550	290	260
Ethyl Corporation	Houston, Texas	260	260	
The B. F. Goodrich Company	Calvert City, Ky.	990	330	660
PPG Industries, Inc.	Lake Charles, La.	1,040	803	237
Shell Chemical Company	Deer Park, Texas	1,700	1,126	574
Union Carbide Corporation	Taft, La.	150	150	
Union Carbide Corporation	Texas City, Texas	150	150	
Vulcan Materials Company	Geismar, La.	330		330
	Total	9,633	5,563	4,070
		% Total	58%	42%

*Oxychlorination facility presently not in operation.

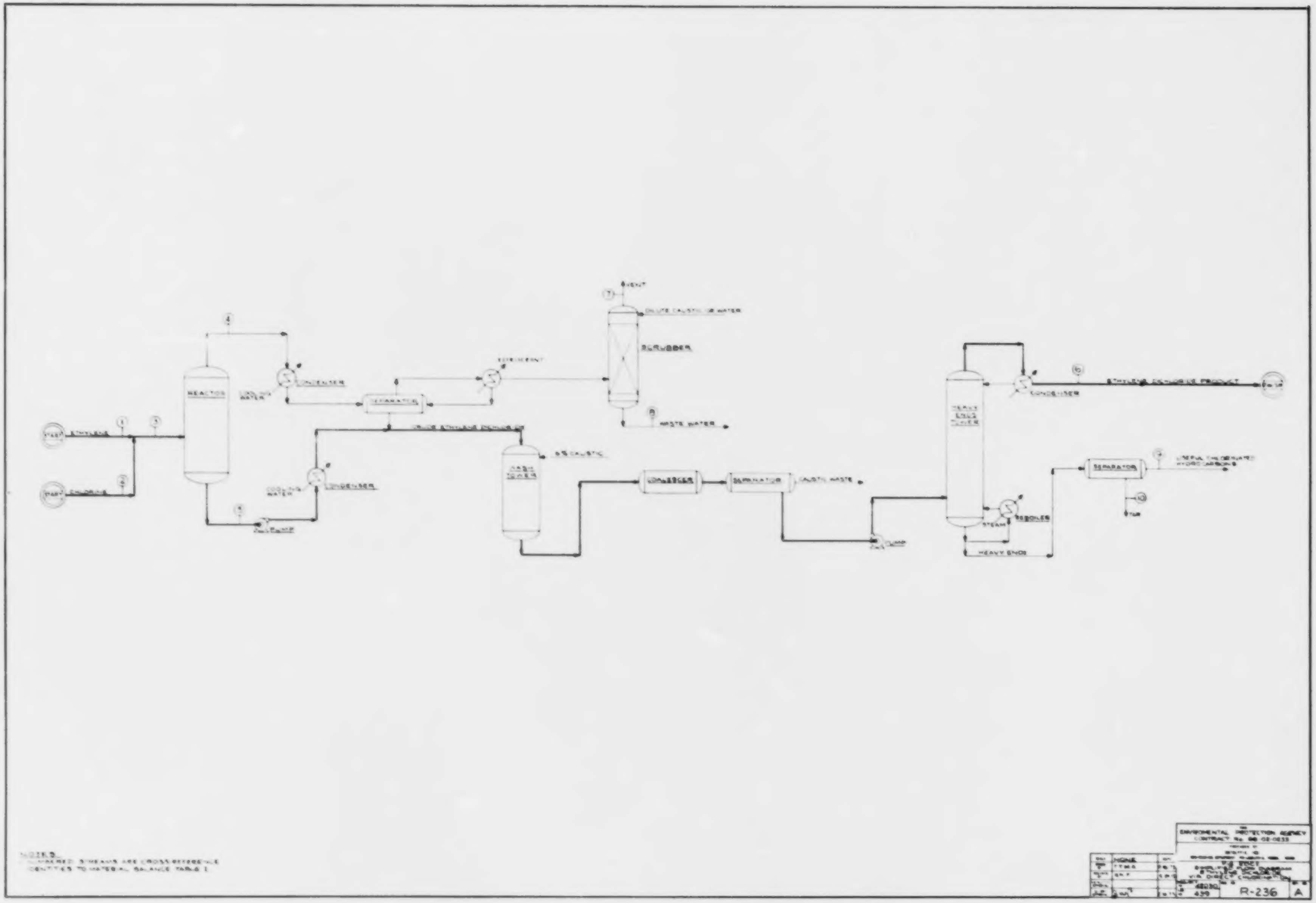
START
ETHYLENE
START
CHLORINE
1
2
3
4
5
REACTOR
COOLING WATER
CONDENSER
PUMP
COOLING WATER
CONDENSER
SEPARATOR
REFRIGERANT
VENT
7
DILUTE CAUSTIC OR WATER
SCRUBBER
8
WASTE WATER
CRUDE ETHYLENE DICHLORIDE
5% CAUSTIC
WASH TOWER
COALESCER
SEPARATOR
CAUSTIC WASTE
PUMP
HEAVY ENDS TOWER
CONDENSER
6
ETHYLENE DICHLORIDE PRODUCT
END
REBOILER
STEAM
HEAVY ENDS
SEPARATOR
9
USEFUL CHLORINATED HYDROCARBONS
10
TAR
NOTES:
1. NUMBERED STREAMS ARE CROSS-REFERENCE IDENTITIES TO MATERIAL BALANCE TABLE 1
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT No. 68-02-0833
SIMPLIFIED FLOW DIAGRAM
ETHYLENE DICHLORIDE
VIA DIRECT CHLORINATION
NONE
48030
439
R-236
A

TABLE EDC-I
MATERIAL BALANCE (LBS./LB. EDC)
ETHYLENE DICHLORIDE
VIA
DIRECT CHLORINATION

Stream I. D. No.	1	2	3	4 & 5	6	7	8	9	10
Stream	Ethylene Feed	Chlorine Feed	Total Feed	Reactor Effluent	Product	Scrubber Vent	Acid, Chlorine & Ethylene Dichloride in Scrubber Waste	Useful Heavy Ends	Tar
Ethylene	.2916		.2916	.0031		.0031			
Chlorine		.7258	.7258	.0001			.0001		
Inerts									
CO_2		.0040	.0040	.0040		.0040			
O_2		.0087	.0087	.0087		.0087			
N_2		.0076	.0076	.0076		.0076			
H_2		.0002	.0002	.0002		.0002			
Ethylene Dichloride				1.0030	.9990	.0022	.0018		
Ethylene Trichloride				.0101	.0010			.0091	
Hydrogen Chloride				.0004			.0004		
Tar				.0007					.0007
	.2916	.7463	1.0379	1.0379	1.0000	.0258	.0023	.0091	.0007

TABLE EDC-II
ENERGY BALANCE (REACTOR SECTION ONLY)
ETHYLENE DICHLORIDE
VIA
DIRECT CHLORINATION

HEAT IN

SOURCE	BTU/LB. EDC
Enthalpy of feed at 110° F (above base temperature)	10
Exothermic heat of reaction (110° F)	956
	Total - 966

HEAT OUT

SOURCE	BTU/LB. EDC
Reactor coolant	956
Enthalpy residual (above base temperature)	10
	Total - 966

NOTE: Base temperature = 60° F

TABLE EDC-III
NATIONAL EMISSIONS INVENTORY
DICHLOROETHANE BY
DIRECT CHLORINATION

Page 1 of 3

EPA Code No.	12-1			
Capacity - Tons of EDC	47,500			
Average Production - Tons of EDC	47,500			
Emissions to Atmosphere				
Stream	Scrubber Vent	Primary Decanter Vent	Secondary Decanter Vent	Fugitive Emissions
Flow - lbs./Hr.	351	100	20	1
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
If Intermittent - Hrs./Yr. Flow				
Composition - Tons/Ton of EDC				
1,2 Dichloroethane	.002675	.000588	.000118	( )
Vinyl Chloride				(.00009)
Ethyl Chloride				( )
Methane				
Ethylene	.003789			
Oxygen	.008658			
Nitrogen	.007579			
Carbon Dioxide	.003965			
Carbon Monoxide				
Water	.000325	.000430	.000086	
Air		.007754	.001550	
Hydrogen Chloride				
Chlorine				
Hydrogen	.000184			
Analysis	No	No	No	
Sample Location				
Date or Frequency of Sampling				
Type of Analysis	Estimate	Estimate	Estimate	
Odor Problem	On-Plant	On-Plant	On-Plant	
Vent Stacks	Yes	Yes	Yes	
Number	1	3	2	
Height - Feet	38	12	20	
Diameter - Inches	4	1.5, 2.25, 2 (1)	1.54, 1.54 (1)	
Exit Gas Temperature - F°	50	90	80	
Flow - SCFM	65	23	4.7	
Emission Control Devices	Yes	No	No	
Condenser				
Water Scrubber	Yes			
Spray Tower				
Total Hydrocarbon Emissions - Ton/Ton EDC	.006464	.000588	.000118	.000091
Total Particulate & Aerosol Emissions - Ton/Ton EDC	0	0	0	0
Total NO_x Emissions - Ton/Ton EDC	0	0	0	0
Total SO_x Emissions - Ton/Ton EDC	0	0	0	0
Total CO Emissions - Ton/Ton EDC	0	0	0	0

(1) Equivalent diameter

TABLE EDC-III
NATIONAL EMISSIONS INVENTORY
DICHLOROETHANE BY
DIRECT CHLORINATION

Page 2 of 3

EPA Code No.	12-2	
Capacity - Tons of EDC	401,500	
Average Production - Tons of EDC	401,500	
Emissions to Atmosphere		
Stream	Scrubber Vent	Scrubber Vent
Flow - Lbs./Hr.	422	702
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow		
Composition - Tons/Ton of EDC		
1,2 Dichloroethane	.000231	.000775
Vinyl Chloride	.000022	.000023
Ethyl Chloride	.000576	.000406
Methane		000812
Ethane	.000157	.000127
Ethylene	.000879	.001476
Oxygen		
Nitrogen		
Carbon Dioxide	.000795	001504
Carbon Monoxide		
Water	.000053	000282
Hydrogen Chloride		
Chlorine		
Air	.001879	.002311
Analysis	Yes	Yes
Sample Location	In Vent	In Vent
Date or Frequency of Sampling	Four times per week for six weeks	Four times per week for six weeks
Type of Analysis	Chromatograph	Chromatograph
Odor Problem	No	No
Vent Stacks	Yes	Yes
Number	1	1
Height - Feet	95	120
Diameter - Inches	.505	.505
Exit Gas Temperature - F°	Ambient	Ambient
Flow - SCFM	75	150
Emission Control Device	Yes	Yes
Condenser		
Water Scrubber	Yes	Yes
Spray Tower		
Total Hydrocarbon Emissions - Ton/Ton EDC	.001865	.002807
Total Particulate & **Aerosol** Emissions - Ton/Ton EDC	0	0
Total NO_x Emissions - Ton/Ton EDC	0	0
Total SO_x Emissions - Ton/Ton EDC	0	0
Total CO Emissions - Ton/Ton EDC	0	0

TABLE EDC-III
NATIONAL EMISSIONS INVENTORY
DICHLOROETHANE BY
DIRECT CHLORINATION

Page 3 of 3

EPA Code No.	31-1	
Capacity - Tons of EDC	238,000	
Average Production - Tons of EDC	Not Specified (1)	
Emissions to Atmosphere		
Stream	Scrubber Vent	Fugitive Emissions
Flow - lbs./Hr.	649	42
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow		
Composition - Tons/Ton of EDC	(2)	
1,2 Dichloroethane	.000156	( )
Vinyl Chloride	.000018	( )
Ethyl Chloride	.000014	(.000706)
Methane	.001232	( )
Ethylene	.000262	( )
Oxygen	.002274	
Nitrogen	.003983	
Carbon Dioxide	.002689	
Carbon Monoxide	.000193	
Water		
Hydrogen Chloride	.000062	
Chlorine	.000020	
Analysis	Yes	None
Sample Location	In Vent	
Date or Frequency of Sampling	Once a week	
Type of Analysis	Chromatograph titration for Cl_2	Estimate
Odor Problem	Yes	No
Vent Stacks	Yes (3)	
Number	1	
Height - Feet	148	
Diameter - Inches	3	
Exit Gas Temperature	90	
Flow - SCFM	11,000	
Emission Control Device	Yes	
Condenser	Yes	
Water Scrubber	Yes	
Spray Tower		
Total Hydrocarbon Emissions - Ton/Ton EDC	.000450	.000706
Total Particulate & Aerosol Emissions - Ton/Ton EDC (4)	.000082	0
Total NO_x Emissions - Ton/Ton EDC	0	0
Total SO_x Emissions - Ton/Ton EDC	0	0
Total CO Emissions - Ton/Ton EDC	0	0

(1) Approximate capacity based on total capacity for oxychlorination and direct chlorination units and approximate oxychlorination capacity.
(2) Approximate composition based on percentage of combined oxychlorination and direct chlorination feed stream to the scrubber and assumption (1)
(3) Unit used by oxychlorination process also
(4) Classifies HCl and Cl_2 as aerosol because both are vapor at emitted conditions.

TABLE EDC-IV
CATALOG OF EMISSION CONTROL DEVICES
DICHLOROETHANE
VIA
DIRECT CHLORINATION

ABSORBERS/SCRUBBERS				
EPA Code No.	12-1	12-2	12-2	31-1
Device I. D. No.	SC-I	SC-II	SC-III	SC-IV (2)
Control Emission of	HCl, Cl_2	HCl, Cl_2	HCl, Cl_2	HCl, Cl_2
Scrubbing Liquid	Water	Water	Water	Water
Type - Spray				Yes
Packed Column	Yes	Yes	Yes	Yes
Column w/trays				
Scrubbing/Absorbing Liquid Rate - GPM	3	35	45	
Operating Temp - F°	40-60	200	200	~100
Gas Rate - SCFM (Lb./Hr.)	65	75	150	150 (3) 11,000 (4)
T-T Height - Feet	9	12	12	50
Diameter - Feet	1.5	3	3	10
Washed Gases to Stack	Yes	Yes	Yes	Yes
Stack Height - Feet	38	95	120	148
Stack Diameter - Inches	4	6.06	6.06	36
Installed Cost - Mat'l. & Labor - $	6,300	12,000		2,900 (5)
Installed Cost based on "year" - dollars	1954	1967		1969 & 1971
Installed Cost - ¢/lb. of Dichloroethane - Yr.	.0066	.0015		.0006
Operating Cost - Annual - $ (1972)	2450	Unknown (1)		672 (5)
Value of Recovered Product - $/Yr.	1250			
Net Operating Cost - Annual - $	1200			0
Net Operating Cost - ¢/lb. of Dichloroethane	.00013			.0001
Efficiency - % - SE (Hydrogen Chloride)	100%			75%
Efficiency - % - SE (Chlorine)	100%			
Efficiency - % - SE (Dichloroethane)	39%			
Efficiency - % - SERR	25%			18%

CONDENSERS AND K. O. DRUMS	
EPA Code No.	31-1
Device I. D. No.	CON-I
Control Emission of	Dichloroethane
Primary Refrigeration Liquid	Freon
Capacity of Refrigeration Liquid - Ton	
Gas Rate - SCFM (Lbs./Hr.)	178
Temperature to Condensers - F°	95
Temperature out of Condensers - F°	-10
Liquid Recovered - Lb./Hr.	304
Non-Condensibles - SCFM	150
Installed Cost - Mat'l. & Labor - $	125,000
Installed Cost based on - "year" - dollars	100,000 - 1967; 25,000 - 1972
Installed Cost - ¢/lb. of Dichloroethane	.026
Operating Cost - Annual - $ (1972)	15,800
Value of Recovered Products - $/Yr.	60,800
Net Operating Cost - Annual - $	(45,000)
Net Operating Cost - ¢/lb. of Dichloroethane	(.0095)
Efficiency - % - SE	97.9%
Efficiency - % - SERR	89.4%

(1) $1200 for utilities only.
(2) Scrubber serves combined streams from oxychlorination and direct chlorination units
(3) From direct chlorination only.
(4) Total to unit.
(5) Calculated by multipling total cost by fraction of in-let from direct chlorination process.

TABLE EDC-V
NUMBER OF DIRECT CHLORINATION ETHYLENE DICHLORIDE PLANTS BY 1980

Current Capacity (1)	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity to be Added	Economic Plant Size	Number of New Units
5,563	300	5,263	11,513	6250 (2)	700	9 - 10

(1) All capacities in MM lbs./year.

(2) Based on the assumption that balanced EDC plants will be built, increasing the present total EDC capacity by 12.5 billion lbs/year.

TABLE EDC-VI
EMISSION SOURCE SUMMARY
TONS/TON OF ETHYLENE DICHLORIDE

Emissions	Source			Total
	Scrubber Vent	Storage Losses	Fugitive Emissions	
Hydrocarbons	.00416	.00060	.00071	.00547
Particulates & Aerosols	0	0	0	0
NO_x	0	0	0	0
SO_x	0	0	0	0
CO	0	0	0	0

TABLE EDC-VII
WEIGHTED EMISSION RATES

Chemical Ethylene Dichloride

Process Direct Chlorination

New Added Capacity 6,250 MM Lbs./Year

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Yr.	Weighting Factor	Weighted Emissions MM Lbs./Yr.
Hydrocarbons	.00547	34.2	80	2.736
Particulates & Aerosols	0	0	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	0	0	1	0

Significant Emission Index = 2,736

Formaldehyde (Silver Catalyst)

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Emission Inventory — Table FS-III
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I. Introduction

Formaldehyde was first produced in the U. S. in 1901, at that time its chief use was as an embalming agent and disinfectant. Today, some seventy odd years later production capacity exceeds seven and one half billion pounds per year, with approximately two thirds of the production utilized in the formulation of various synthetic resins.

Formaldehyde is normally marketed in aqueous solutions containing from 36 to 50 weight percent formaldehyde. The standard (USP) solution is 37 percent, although large scale industrial users prefer a nominal 50 percent solution. Formaldehyde solutions usually contain sufficient methanol to prevent precipitation of polymer during storage and shipping, although precipitation may be prevented in solutions containing relatively small amounts of methanol by keeping the solution warn.

Formaldehyde is produced principally from methanol. Two processes are dominant in the U. S. today, the mixed oxide catalyzed process and the silver crystal (or gauze) catalyzed process.

The primary licensors of the mixed oxide process are Reichhold and Lummus, while ICI and Borden prevail in the licensing of the silver process. The silver catalyzed process is the subject of this report.

A third process, based on the partial oxidation of light hydrocarbons, had been utilized by Celanese at their large Bishop, Texas plant until quite recently. That particular facility at Bishop has now been shutdown and replaced by a silver process unit. With national energy source demands escalating feedstock costs for the partial oxidation process, it is extremely doubtful that any new facility in the U. S. will again employ this process, in spite of rising methanol costs.

Atmospheric emissions generated by the silver catalyst process are associated primarily with the absorber vent gas stream. Minor quantities of hydrocarbons may be discharged by steam ejectors on the product fractionator. Additionally, small quantities of spent caustic or waste water may be produced.

Today an estimated 77 percent of U. S. formaldehyde capacity is based on the silver catalyst process. This is appreciably more than its estimated share of 61 percent in 1969. A large part of this increase is due to Celanese switching to the silver process, but even discounting that situlation, the capacity of the silver-catalyzed process appears to be increasing at a faster rate than does the capacity of the mixed oxide process. If the silver process can maintain its present share of the total formaldehyde capacity, it will expand to 8 x 10^9 pounds per year in 1980.

II. Process Description

Despite the fact that formaldehyde was produced from methanol over one hundred years ago (in 1868 by A. W. Hofmann), the chemistry - of the silver catalyzed process - is still in dispute. It is thought that the reaction involves either the dehydrogenation of methanol (EQ. 1) followed by the oxidation of hydrogen (EQ. 2A).

(1) $CH_3OH \rightleftharpoons CH_2O + H_2$

(2A) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

or a combination of methanol dehydrogenation (EQ. 1) and methanol oxidation (EQ. 2B)

(1) $CH_3OH \rightleftharpoons CH_2O + H_2$

(2B) $CH_3OH + \frac{1}{2} O_2 \longrightarrow CH_2O + H_2O$

Regardless of this controversy, the implementation of the process is relatively simple and quite straightforward, as evidenced by the following brief process description (which may be more easily followed by referring to the Figure I flow sheet):

> Prior to its admixture with methanol vapors, air is caustic washed to remove CO_2 and trace sulfur compounds - the latter of which will poison the silver catalyst. The air is then heated to about 150° F.
>
> Fresh methanol and recycle methanol are combined, vaporized and then superheated to approximately 170° F. Heat is supplied by either exchange with the converter effluent or medium pressure steam.
>
> The air and methanol vapors are combined to give about a 1:4 oxygen/methanol mole ratio. (Decreasing the percentage of methanol in the mixture decreases conversion while increasing yield; however, methanol must comprise more than 37 percent by volume of the mixture to avoid the explosive area. Increasing the amount of methanol increases conversion and decreases yield.) The air/methanol mixture is induced into a battery - sometimes about three - of catalytic converters. Upon passing through the silver catalyst, the net exotherm generated heats the vapors to about 1175° F. This temperature is maintained either by varying the air/methanol ratio or by means of combination heating and cooling coils located within the converters. The hot effluent gases must be quenched to avoid decomposing the formaldehyde. This is generally accomplished solely within the primary absorber, which is close-coupled with the converters, but feed vs effluent heat exchange is utilized - in part - by some plants.
>
> The primary absorber is a packed tower. The primary absorption liquid - and quench - for the formaldehyde and unreacted methanol vapors is the so-called "F-M Liquor". This liquor is an aqueous solution containing about 28 to 30 percent formaldehyde and 20 to 22 percent methanol. Part of the FM liquor is withdrawn from the bottom of the primary absorber, pumped through a water cooled exchanger, and recirculated to the top of the primary absorber. The remainder of the FM liquor is withdrawn from the bottom of the absorber and pumped to intermediate storage. Uncondensed vapors and non-condensibles are withdrawn from the top of the primary absorber and 'blown' into the secondary absorber.

The secondary absorber recovers the major portion of the uncondensed vapors by providing the necessary contact between the vapors and cool distilled water, which is introduced onto the top tray of the secondary absorber. The top of the tower is maintained at about 75° F to 80° F by providing additional cooling via secondary coolers for the upper tray section. This minimizes hydrocarbon loss via the relatively large non-condensible overhead vent. The weak formaldehyde/methanol solution withdrawn from the bottom of the secondary absorber is pumped to the primary absorber and used as make-up.

The FM liquor in the intermediate storage or surge tank is pumped to the product fractionator - a vacuum column. Here pure (99 + %) methanol is taken as overhead product and recycled to either methanol storage or to the vaporizer. The bottom product is a nominal 37 wt. % solution of formaldehyde, containing less than one percent methanol. This solution may be treated for removal of trace amounts of formic acid prior to storage. Polymer formation and precipitation in storage is prevented either by the addition of supplemental methanol, by providing heated storage, or by both.

Table FS-I presents a typical material balance for silver process formaldehyde production. Absorber vent gas composition is based on a combination of published data and questionnaire responses, whereas the below listed yields, etc., are representative of published data only:

	Mole %
Methanol in air/methanol feed mixture	44
Methanol conversion	65
Formaldehyde yield (F.F. basis)	89

Table FS-II presents an estimated heat balance around the converter section.

III. Plant Emissions

A. Continuous Air Emissions

1. Absorber Vent

The emissions from this vent constitute the most important source of air pollution associated with the production of formaldehyde. Indeed, many respondents report it as their sole source of noxious emissions.

The composition of the absorber vent stream varies somewhat with catalyst age or activity. The normal range in composition (excluding for the moment uncondensed hydrocarbons) is*:

Component	Vol. % (dry basis)
CO_2	4.8 to 5.5
CO	0.2 to 0.6
CH_4	0.3 to 0.4
O_2	0.3
H_2	20.2 to 17.5
N_2	74.2 to 75.7

These reaction by-products transport varying quantities of hydrocarbons to the atmosphere when they are vented. Respondents report the following hydrocarbon emissions are associated with their absorber vents.

Component	Amount Lb./Lb. of 37% HCHO
Formaldehyde	0 to .001
Methanol	0 to .004
Methyl Formate	0 to .008
Methylal	0 to .001

A more complete summary of these emissions is listed in Table FS-III

2. Product Fractionator Ejector Exhaust

It is believed that all product fractionators are operated at sub-atmospheric pressures, which, therefore, requires the use of either steam ejectors or vacuum pumps. Four respondents reported emissions from this source, but only three (EPA Code No's. 14-4, 14-8 and 14-20) reported the emission of noxious compounds. The emissions from the ejectors are listed in Table FS-III.

B. Intermittent Air Emissions

1. Converter Start-Up Vent

The operator of plant EPA Code No. 14-3 reported emissions from this source and stated that, "during start-ups the feed to to converter is vented to the atmosphere until stabilized and then switched gradually into the reactor. Total vent time is about 30 minutes. There are about 10 start-ups per year". Data provided by the respondent indicate that this operation results in the emission of .0001 lbs. of hydrocarbons per lb. of formaldehyde.

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*"Formaldehyde" - 3rd Edition, ASC Monograph Series, page 18

Start-up vents of a different nature were reported by respondents 14-6 and 14-9, both of whom burn their absorber tail gases in the boiler house. During start-ups, until the tail gas composition and flow have stabilized, the tail gas is vented to the atmosphere. After this period the tail gas is cut to the boiler house and burned. No estimate was given of the emissions resulting from this operation, but they should be negligible.

2. Converter Emergency Vent

Again, only operator 14-3 reported emissions from this source. Lack of data prevents the calculation of emission rates, but the infrequency and short duration of the emission preclude its characterization as a significant emission source.

C. Continuous Liquid Wastes

1. Waste Water

The production of various waste water streams have been reported as follows:

Plant 14-3 - .030 gallons/lb. of 37% formaldehyde or 360 gallons/hour. The waste is treated on plant in an extended aeration biological treatment plant.

Plant 14-7 - 62,500 gallons/hour of cooling water. 'Treated' on plant.

Plant 14-8 - 120 gallons/hour from the waste heat boiler blowdown plus 4500 gallons/hour from the cooling tower blowdown.

Plant 14-20 - 7500 gallons/hour cooling tower blowdown. Treated on plants.

2. Spent Caustic

While no operator reported the generation of spent caustic, it seems reasonable to surmise that most plants do produce small quantities of this substance as a result of their air washing operation.

D. Intermittent Liquid Wastes

1. Ion Exchange Regeneration

Presumably most operators remove formic acid from product formaldehyde via an ion exchange resin system. Such systems are normally regenerable by intermittent back-flushing procedures, which would produce an intermittent waste liquid stream. Operator 14-10 reports that every six to twenty days a weak aqueous solution containing about 0.4% formic acid and 1.5% formaldehyde is discharged to the waste treatment plant as a result of this operation. Flow rates are not given. Operator 14-3 shows such a waste stream on this block flow diagram, but given no further details in the body of his response.

2. Methyl Formate Removal

One operator reported privately that it was his practice to remove methyl formate from stored formaldehyde. Presumably, this would result in the production of a small intermittent liquid waste stream. It is believed that this operation is atypical of the industry.

3. Tank Washings

This is another verbally reported source of intermittent liquid wastes.

E. Solid Wastes

All respondents to the silver process questionnaire reported that their facility produced no solid waste material.

F. Odors

None of the respondents reported receiving any odor complaints during the past year. Half of the respondents, however, did report that odors are occasionally detectable at the plant site. The odoriferous materials were identified as formaldehyde and methanol.

All operators reporting odors mentioned the absorber vent as at least one of the sources. In addition, operators 14-3 and 14-8 identified the product fractionator as a source.

G. Fugitive Emissions

Only the operator of plant 14-3 has offered a quantitative estimate of fugitive emissions. His estimate is 30 lbs./hr. or .00025 lbs./lb. All other operators state that fugitive emissions are either nil or quite small. As operator 14-4 summarizes the situation, "minor losses of formaldehyde and/or methanol occur mainly due to leaks in pump seals and occasional piping leaks. The actual amount is considered negligible and most likely will not show in material balance calculations".

IV. Emission Control

The few emission control devices that were reported as being employed, by respondents to the questionnaires pertaining to the subject process, are summarily described in Table IV of this report. An efficiency has been assigned each device when data sufficient to calculate it have been available. Three types of efficiency are normally calculated:

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{lbs. of specific pollutants in} - \text{lbs. of specific pollutant out}}{\text{lbs. of specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR}^* = \frac{(\text{lbs. of pollutant} \times \text{wf})\text{in} - (\text{lbs. of pollutant} \times \text{wf})\text{out}}{(\text{lbs. of pollutant} \times \text{wf})\text{in}} \times 100$$

*where wf = weighting factor designated in Table VII of this report

Usually a combustion type control device (i.e., incinerator, flare, etc.) will be assigned both a "CCR" and a "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in the (revised) Appendix V of this report.

Since data sufficient to permit device efficiency calculation are available for only one device, a few general comments regarding formaldehyde pollution control device performance seem in order:

Absorber/Scrubbers

The only reported scrubber (Plant 14-4) uses water as the scrubbing medium in a bubble cap tower for methanol and formaldehyde removal. No data are given, but the efficiencies should be near 100 percent.

Mist Eliminators

Devices FS-3, 4 and 5 have rather arbitrarily been listed under "absorbers/scrubbers" in Table IV - Catalog of Emission Control Devices. All are simple wire gauze mist eliminators located in the top of the absorber. They undoubtedly are reasonably efficient in preventing the emission of entrained liquids, however, no respondent has provided data from which efficiencies might be calculated. Due to the diversity and range of the parameters governing their performance, it would be imprudent to attempt to further characterize them with an estimate of their performance.

Incinerators

Two respondents report burning 'tail gas' (absorber vent gas) as a method of controlling associated noxious emissions. Since the compounds being burned are 'straight' organics, containing no heteroatoms, one would expect his method to be quite efficient - and it presumably is. The operator fo EPA Coded Plant No. 14-1 utilizes an in-house designed incinerator (Device FS-1) to burn tail gas. Data provided by him indicate that this device has "CCR" and "SERR" efficiencies of 100 percent. Respondent 14-9 combusts tail gases in another in-house designed device - this one a custom burner for the boiler house (Device FS-2). The respondent considers the performance data for his boiler house tail gas burner proprietary, but it seems reasonable to surmise that it is highly efficient.

From a technical view point, it would seem that incineration devices are ideally suited for minimizing the pollutant nature of the principal atmospheric emission generated by the subject process.

Condensers

The operator of plant EPA Code No. 14-8 lists a refrigerated condenser (Device FS-6), which is located up-stream of the product fractionator vacuum ejector, as a pollution control device. The condenser undoubtedly reduces the quantity of methanol discharge to the atmosphere. It would seem, however, that this device might more properly be considered a part of the methanol recovery equipment rather than a pollution control device, although industry is not in full agreement on this point. The distinction between the two is difficult, but based on data provided by other respondents, most plants apparently employ similar conservation devices and have chosen not to designate them pollution control devices.

Operating the 'silver catalyst' formaldehyde process at lower air/methanol ratios should reduce ghe quantity of hydrocarbons discharged to the atmosphere via the absorber vent. However, as pointed out in Section I, decreasing this ratio (i.e., increasing the methanol concentration in the feed gas) decreases conversion. There is undoubtedly a point where the net heat of reaction would fail to sustain the process without a supplemental heat source. This would probably be quite unattractive to most operators. Considering the relatively low emission rate associated with the process, and the effectiveness of tail gas incineration, it wold seem that such manipulation of operating variables to achieve lower levels of atmospheric emissions is unnecessary. Changing of operating temperature and/or pressure would also be unattractive, since current conditions are considered to be "close to optimum".

Developmental work directed toward reducing emissions from this process might be directed along the following lines:

(1) Substitute oxygen for air and dilute with tail gas to achieve desired heat balance.

(2) More efficient design and better utilization of control devices currently available.

V. Significance of Pollution

It is recommended that the silver catalyst process be considered for an in-depth study. Although the Significant Emission Index rating is normally the criterion for this recommendation, in this instance there are other factors of overriding importance. They are:

(1) A large number of new units 18-19 are expected to be on-stream by 1980.

(2) The absorber vent gas has a wide heating value range, but normally is able to support combustion without supplementary fuel.

(3) Although not classified as a source of odor problems, the uncombusted tail gas is odoriferous.

(4) Only a small percentage of formaldehyde plant operators burn tail gas.

(5) Increased emission control through tail gas combustion would conserve national energy sources, if the heat so produced is recovered.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

The 1980 production capacity estimate is based on the assumption that the silver catalyst process will account for the same 77 percent of total capacity that it does now - see Section VI. Published support for the estimate of 1980 production capacity (total) may be found in the May 1st issue of Chemical Marketing Report and the August, 1970 Chemical Economics Handbook report on formaldehyde.

On a weighted emission basis, a Significant Emission Index of 1,251 has been calculated in Table VII. Although this is appreciably less than the SEI's anticipated for some of the other processes in the study, it is believed the above listed reasons justify the recommendation for an in-depth study of the process.

VI. Formaldehyde Producers

The following tabulation of formaldehyde producers indicates published production capacity by company, location and process.

Company	Location	Silver Process	Metal Oxide Process
Allied	Ironton, Ohio	308	
Borden	Demopolis, Ala.	80	
	Diboll, Texas	70	
	Fayetteville, N. C.	200	
	Fremont, Calif.	80	
	Kent, Wash.	70	
	La Grande, Oregon	40	
	Louisville, Ky.	70	
	Missoula, Mont.	80	
	Sheboygan, Wisc.	120	
	Springfield, Oregon	260	
Celanese	Bishop, Texas	1300	
	Newark, N. J.		117
	Rock Hill, S. C.		117
Commercial Solvents	Sterlington, La.	30	
	Seiple, Pa.	80	
Du Pont	Belle, W. Va.	485	
	Grasselli, N. J.	150	
	Healing Spring, N. C.	200	
	La Porte, Texas	200	
	Toledo, Ohio	320	
	Linden, N. J.	150	
GAF	Calvert City, Ky.		100
Georgia Pacific	Columbus, Ohio		100
	Coos Bay, Oregon		80
	Crosett, Ark.	100	60
	Albany, Oregon		100
	Taylorsville, Miss.		100
	Vienna, Ga.	100	
Gulf	Vicksburg, Miss.		40
Hercules	Louisiana, Mo.	170	
	Wilmington, N. C.	95	
Hooker	N. Tonawanda, N. Y.	135	
Monsanto	Alvin, Texas	150	
	Addyston, Ohio	110	
	Eugene, Oregon	100	
	Springfield, Mass.	280	

Company	Location	Silver Process	Metal Oxide Process
Reichhold	Hampton, S. C.	36	
	Houston, Texas		100
	Moncure, N. C.		100
	Tacoma, Wash.		40
	Tuscaloosa, Ala.	70	
	Kansas City, Kans.	40	
	White City, Oregon		50
	Malvern, Ark.		100
Rohm & Haas	Philadelphia, Pa.	25	
Skelly	Springfield, Oregon		70
	Winfield, La.		70
Tenneco	Fords, N. J.	105	160
	Garfield, N. J.	105	
Union Carbide	Bound Brook, N. J.		150
Wright	Acme, N. C.		75

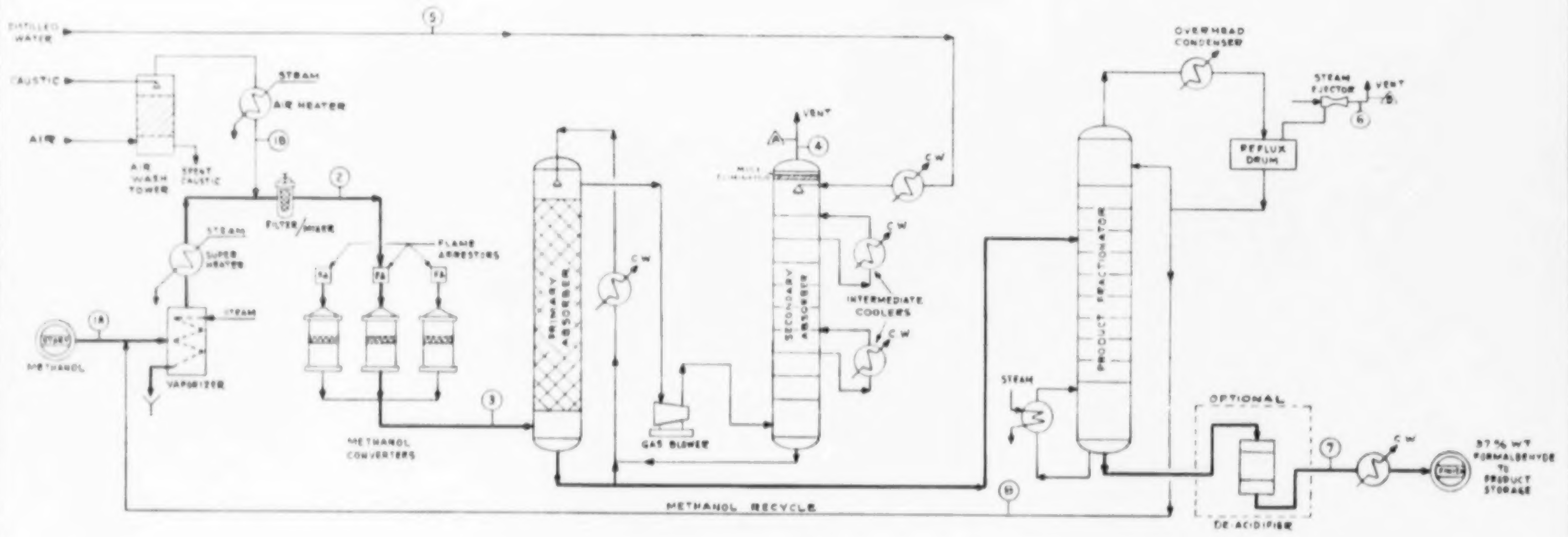
Total Process Capacity - MM Lbs./Year = 5,914 1,729

Number of Plants = 36 18

Average Plant Size - MM Lbs./Year = 165.4 98.2

Capacity of Total Industry - MM Lbs./Year = 7,613

Percentage of Total Industry Capacity = 78.2 21.9


DISTILLED WATER
CAUSTIC
AIR
AIR WASH TOWER
SPENT CAUSTIC
STEAM
AIR HEATER
STEAM
SUPER HEATER
STEAM
VAPORIZER
METHANOL
FILTER/MIXER
FLAME ARRESTORS
FA
FA
FA
METHANOL CONVERTERS
PRIMARY ABSORBER
CW
GAS BLOWER
VENT
MIST ELIMINATOR
SECONDARY ABSORBER
CW
CW
CW
INTERMEDIATE COOLERS
METHANOL RECYCLE
STEAM
PRODUCT FRACTIONATOR
OVERHEAD CONDENSER
REFLUX DRUM
STEAM EJECTOR
VENT
OPTIONAL
DE-ACIDIFIER
CW
37% WT FORMALDEHYDE TO PRODUCT STORAGE
5
1B
1A
2
3
4
A
6
B
8
7

NOTES:

1. REFER TO TABLE IV - CATALOG OF EMISSION CONTROL DEVICES - FOR DESCRIPTION OF DEVICE LOCATED AT LETTERED SITES; FOR EXAMPLE, A
2. REFER TO TABLE I - MATERIAL BALANCE - FOR DESCRIPTION OF NUMBERED STREAMS

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO 68-02-0255

PREPARED BY
CATALYTIC, INC
ENGINEERING DEPARTMENT PHILADELPHIA, PENNA. [illegible]

FIGURE PS-1
SIMPLIFIED FLOW DIAGRAM
FORMALDEHYDE PRODUCTION VIA METHANOL OXIDATION AND DEHYDROGENATION (SILVER CATALYST PROCESS)

SCALE	NONE	DATE
DRAWN BY	ECA	8/1/73
CHECKED BY	[illegible]	[illegible]
CATALYTIC APPROVAL		
CLIENT APPROVAL	[illegible]	[illegible]

PROJECT NO. 42030
J.O. NO. 419
DWG NO. R-216
REV. A

TABLE 15-1
TYPICAL MATERIAL BALANCE
FOR
SILVER CATALYST PROCESS FORMALDEHYDE PLANT

UNITS - TON/TON OF 37% FORMALDEHYDE

Stream I. D. No.	1 (A & B)	2	3	4	5	6	7	8
	Fresh Feed	Total Feed	Methanol Converter Effluent	Absorber Vent Gas	Absorber Make-up Water	Product Fractionator Vent*	Product	Product Fractionator Liq. Ovhd. - Recycle**
Formaldehyde			.3709	.0006		.0003	.3700	
Methanol	.4430	.6675	.2328	.0025		.0008	.0050	.2245
Hydrogen			.0100	.0100				
Carbon Dioxide			.0455	.0455				
Carbon Monoxide			.0052	.0052				
Water			.1763	.0145	.4632		.6250	
Oxygen	.1763	.1763	.0031	.0031				
Nitrogen	.5832	.5832	.5832	.5832				
Total	1.2025	1.4270	1.4270	.6646	.4632	.0011	1.0000	.2245

*Also contains steam from ejector (when used) and water vapor and air from leakage.

**Contains unknown amount of formaldehyde.

TABLE FS-II
FORMALDEHYDE PRODUCTION
VIA
SILVER CATALYST PROCESS

GROSS HEAT BALANCE - CONVERTER SECTION ONLY

Heat In	BTU/Lb. of 37% Formaldehyde
Air Heater	23
Methanol Heater, Vaporizer and Superheater	364
Exothermic Heat of Reaction	1,022
	Total - 1,409

Heat Out	
Converter Temperature Control	100
Endothermic Heat of Reaction	441
Converter Effluent Quench plus Enthalpy Residual (above base temp.)	868
	Total - 1,409

Note:

(1) Based on air/methanol and oxidation/dehydrogenation ratios shown in Table I.

(2) Converter temperature - 1175° F.

(3) Base temperature - 60° F.

TABLE FS-III
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

Page 1 of 6

EPA Code Number	14-1		14-3	
Date on-stream				
Capacity - Tons of 37% HCHO/Yr.	154,000		47,500	
Average Production - Tons of 37% HCHO/Yr.			47,500	
Range in Production - % of Max.	17		0	
Emissions to Atmosphere				
Stream	Absorber Vent	Converter Emergency Vent	Converter Start-up Vent	Absorber Vent
Flow - lbs./hr	Not Specified	Not Specified	2620	Not Specified
Flow Characteristic - Continuous or Intermittent	Continuous	Intermittent	Intermittent	Continuous
If Intermittent - hrs/yr.		0.10	5	
Composition - Tons/Ton of 37% HCHO				
Formaldehyde		+		.00114
Methanol		+	.00011	.00364
Methyl Formate				
Di-methyl Ether				
Methylal				
Oxygen				+
Nitrogen				+
Carbon Monoxide				.00159
Carbon Dioxide	+			+
Methane				
Water	+	+	.00003	.01193
Hydrogen				.00755
Sample Tap Location	None	None	None	
Date or Frequency of Sampling	Never	Never	Never	
Type of Analysis				
Odor Problem	No			
Vent Stacks	Yes	Not Specified	Not Specified	Yes
Flow - SCFM per stack				718
Number	1			1
Height - Feet (elev. @ tip)	43.8			6 (68)
Diameter - Inches	42			.67
Exit Gas Temperature - F°		>500°		82°
Emission Control Devices	Yes	No	No	No
Type - Water Scrubber				
Incinerator	X			
Catalog I. D. No.	FS-1			
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	Not Specified		.00489	
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)			0	
Total NO_x - Ton/Ton HCHO (37%)			0	
Total SO_x - Ton/Ton HCHO (37%)			0	
Total CO - Ton/Ton HCHO (37%)			.00159	

TABLE FS-III
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

Page 2 of 6

EPA Code No.	14-4			
Date on-stream				
Capacity - Tons of 37% HCHO/Yr.	52,500			
Average Production - Tons of 37% HCHO/Yr.	52,500			
Range In Production - % of Max.	0			
Emissions to Atmosphere				
Stream	Absorber #1 Vent	Absorber #2 Vent	Absorber #3 Vent	Stripper Overhead Vent
Flow - lbs./hr.	4040	1350	4040	54
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - hrs./yr				
Composition - Tons/Ton of 37% HCHO				
Formaldehyde	.00035	.00012	.00035	.00002
Methanol	.00111	.00037	.00111	.00005
Methyl Formate				
Di-methyl Ether				
Methylal				
Oxygen	.00269	.00090	.00269	+
Nitrogen	.25569	.08523	.25569	+ .00372
Carbon Monoxide	.00238	.00080	.00238	
Carbon Dioxide	.03354	.01115	.03354	+
Methane				
Water	.00946	.00315	.00946	.00038
Hydrogen	.00523	.00174	.00523	
Sample Tap Location	None		None	None
Date or Frequency of Sampling	Never	Never	Never	Never
Type of Analysis	Calc.	Calc.	Calc	Estimate
Odor Problem	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow - SCFM per stack	1090 to 1152	363 to 384	1090 to 1152	5 to 20
Number	1	1	1	1
Height - Feet (elev. @ tip)	60	50	65	65
Diameter - Inches	9	6	9	4
Exit Gas Temperature - F°	104° to 140°	104° to 140°	104° to 140°	78° to 110°
Emission Control Devices	No	No	No	No
Type - Water Scrubber				
Incinerator				
Catalog I. D. No.				
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	.00348			
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)	0			
Total NO_x - Ton/Ton HCHO (37%)	0			
Total SO_x - Ton/Ton HCHO (37%)	0			
Total CO - Ton/Ton HCHO (37%)	.00556			

TABLE FS-III
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

Page 3 of 6

EPA Code Number	14-7	14-8		14-9	
Date on-stream					
Capacity - Tons of 37% HCHO	50,000	25,000		30,919	
Average Production - Tons of 37% HCHO		25,000		30,919	
Range in Production - % of Max.	0	0		0	
Emissions to Atmosphere					
Stream	Absorber Vent	Absorber Vent	Jet Exhaust	Absorber Emerg. Vents Manual/Auto	Absorber Vent
Flow - lbs./hr.	2369	11,600	6		Not Specified
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent	
If Intermittent - hrs./yr					
Composition - Tons/Ton of 37% HCHO					
Formaldehyde	.00035				
Methanol	.00340	.00067	.00033		
Methyl Formate	.00230				
Di-methyl Ether					
Methylal					
Oxygen				+	
Nitrogen	.53000	.56129		+	
Carbon Monoxide	.00100	.00529		+	
Carbon Dioxide	.03850	.05920		+	
Methane					
Water	.02750	.00634			
Hydrogen	.01100	.01263		+	
Sample Tap Location	None	Stack	None	Process	
Date or Frequency of Sampling	Never	1972	Never	Random	
Type of Analysis	Calc'd ex Design	GLC + Titration	Calc'd	Orsat + ?	
Odor Problem	No	No	No	No	
Vent Stacks	Yes	Yes	Yes	Yes	
Flow - SCFM per stack	2000	3200			
Number	1	1	1	1/1	
Height - Feet (elev. @ tip)	98	100	43	30/20	
Diameter - Inches	8	16	1.5	8/8	
Exit Gas Temperature - F°	95	54	200	50°/50°	
Emission Control Devices	Yes	Yes	Yes	No	Yes
Type - Water Scrubber					
Incinerator					+
Demister	+	+			
Other			+ (condenser)		
Catalog I. D. No.	FS-3	FS-5	FS-6		FS-2
Total Hydrocarbon Emissions - Ton/Ton of 37% HCHO	.00605	00100		Not Specified	
Total Particulate & Aerosol Emissions - Ton/Ton of 37% HCHO	0	0			
Total NO_x Emissions - Ton/Ton of 37% HCHO	0	0			
Total SO_x Emissions - Ton/Ton of 37% HCHO	0	0			
Total CO Emissions - Ton/Ton of 37% HCHO	.00100	.00529			

TABLE FS-III
NATIONAL EMISSION INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code Number	14-10	14-9
Capacity - Tons of 37% HCHO/Yr	240,000	200,000
Average Production - Tons of 37% HCHO/Yr		
Range in Production - % of Max	0	0
Emissions to Atmosphere		
Stream	Absorber Vent Incinerator Flue gas	Not Specified
Flow - lbs./hr.	39,722	
Flow Characteristic - Continuous or Intermittent	Continuous	
If Intermittent - hrs./yr.		
Composition - Tons/ton of 37% HCHO		
Formaldehyde	TR	
Methanol	TR	
Methyl Formate		
Di-methyl Ether		
Methylal		
Oxygen	.01005	
Nitrogen	.47940	
Carbon Monoxide		
Carbon Dioxide	.04269	
Methane		
Water	.18491	
Hydrogen	TR	
Sample Tap Location		
Date or Frequency of Sampling	Never	
Type of Analysis	GLC	
Odor Problem	No	
Vent Stacks	Yes	
Flow - SCFM per stack	10,050	
Number	1	
Height - Feet (elev. @ tip)	85	
Diameter - Inches	60	
Exit Gas Temperature - F°	900	
Emission Control Devices	Yes	Yes
Type - Water Scrubber		
Incinerator	+	+ Boiler
Catalog I. D. Number	FS-7	FS-6
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	0	Cannot Be Determined
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)	0	
Total NO_x - Ton/Ton HCHO (37%)	0	
Total SO_x - Ton/Ton HCHO (37%)	0	
Total CO - Ton/Ton HCHO (37%)	0	

TABLE FS-III
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code No.	14-12	14-18		14-20	
Date on-stream					
Capacity - Tons of 37% HCHO	35,000	20,000		50,000	
Average Production - Tons of 37% HCHO	35,000	20,000		50,000	
Range in Production - % of Max.	0	0		0	
Emissions to Atmosphere					
Stream	Absorber Vent	Jet Exhaust	Absorber Vent	Absorber Vent	Distillation Tower Overhead Vent
Flow - lbs./hr.	5,855	1000	3360	7386	30
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
If Intermittent - hrs./yr					
Composition - Tons/Ton of 37% HCHO					
Formaldehyde	.00041			.00035	.00120
Methanol	.00082			.00326	.00120
Methyl Formate				.00224	
Di-methyl Ether					
Methylal					
Oxygen			.00250		
Nitrogen			.54828	.51016	
Carbon Monoxide	.00276		.00292	.00104	
Carbon Dioxide			.05856	.03688	
Methane	.00191		.00167		
Water		.18519		.02656	
Hydrogen	.01390		.00989	.01040	
Sample Tap Location		None	Top of Tower		
Date or Frequency of Sampling	Daily	Never	Bi-annual	Random	Never
Type of Analysis	Calc'd		Orsat + ?	Calc'd	Not Specified
Odor Problem		No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes	
Flow - SCFM per stack	460		891		
Number	1	1	1	1	1
Height - Feet (elev. @ tip)	73	22	44	95	95
Diameter - Inches	18	1	6	132	132
Exit Gas Temperature - F°	80	200	50	95	95
Emission Control Devices	Yes	No	No	No	No
Type - Water Scrubber					
Incinerator					
Demister	+				
Other					
Catalog I. D. No.	FS-4				
Total Hydrocarbon Emissions - Ton/Ton of 37% HCHO	.00123	0		.00825	
Total Particulate & Aerosol Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total NO_x Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total SO_x Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total CO Emissions - Ton/Ton of 37% HCHO	.00276	.00292		00104	

TABLE FS-111
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

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EPA Code No.	14-11	14-20	
Date on-stream			
Capacity - Tons of 37% HCHO/Yr.	427,500	50,000	
Average Production - Tons of 37% HCHO/Yr.		50,000	
Range in Production - % of Max	0	0	
Emissions to Atmosphere			
Stream	Absorber Vent	Absorber Vent	Distillation Tower Overhead Vent
Flow - lbs./Hr.	54,640	2386	30
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr.			
Composition - Tons/Ton of 37% HCHO			
Formaldehyde	<.00001	.00035	00120
Methanol	.00076	.0326	00120
Methyl Formate	.00829	.00224	
Di-methyl Ether			
Methylal	.00120		
Oxygen			
Nitrogen	.396975	.51016	
Carbon Monoxide	.021010	.00104	
Carbon Dioxide	.092096	.03688	
Methane	.000126		
Water		.02656	
Hydrogen	.016271	.01040	
Sample Tap Location	Ground Level		
Date or Frequency of Sampling	Daily	Random	Never
Type of Analysis	Chromatograph	Calc'd	Not Specified
Odor Problem	No	No	No
Vent Stacks	Yes	Yes	
Flow - SCFM per stack	4200 3600 10,000		
Number	1 1 1	1	1
Height - Feet (elev. of tip)	90 93 95	95	95
Diameter - Inches	10 12 14	132	132
Exit Gas Temperature - F°	50 50 50	95	95
Emission Control Devices	No	No	No
Type - Water Scrubber			
Incinerator			
Catalog I. D. No.			
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	01025	00825	
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)		0	
Total NO_x - Ton/Ton HCHO (37%)		0	
Total SO_x - Ton/Ton HCHO (37%)		0	
Total CO - Ton/Ton HCHO (37%)	.02101	00104	

TABLE FS-12
CATALOG OF EMISSION CONTROL DEVICES
FORMALDEHYDE VIA THE SILVER CATALYST PROCESS

Page 1 of 2

ABSORBER/SCRUBBERS				
EPA Code No. for plant using	14-4	14-7	14-12	14-8
Flow diagram (Fig. I) stream I. D.	B	▲	▲	▲
Device I. D. No.	FS-8	FS-3	FS-4	FS-5
Control Emission of	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol
Scrubbing/Absorbing liquid	Water	N/A	N/A	N/A
Type - Spray				
Packed Column	1			
Column w/trays	2			
Number of trays	12 & 14			
Tray type	Bubble Cap			
Other		+ Demister	+ Demister	+ Demister
Scrubbing/Absorbing liquid rate - GPM	5	None	None	None
Design Temp. (Operating Temp.) F°			(80)	(54)
Gas Rate, SCFM (lb./hr.)		2,000	1,460	3,200
T-T Height, Ft.	8 to 15			
Diameter, Ft.	12 to 16			
Washed gases to stack	Yes	Yes	Yes	Yes
Stack height - Ft.		98	73	100
Stack Diameter - Inches		8	18	16
Installed Cost - Mat'l. & Labor - $	Not Available ↓		5,000	700
Installed Cost based on - "year" - dollars			1972	1971
Installed Cost - ¢/lb. of 37% HCHO - Yr.			.00714	.00047
Operating Cost - Annual - $ - 1972				400
Value of Recovered product, $/Yr.		1,440		0
Net Operating Cost - Annual, $				400
Net Operating Cost - ¢/lb. of 37% HCHO				.00027
Efficiency - % - SE				
Efficiency - % - SERR				

INCINERATION DEVICES				
EPA Code No. for plant using	14-1	14-6	14-9	14-10
Flow Diagram (Fig. I) stream I. D.	▲	A	▲	A
Device I. D. No.	FS-1	FS-6	FS-2	FS-7
Type of Compound Incinerated	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol
Type of Device - Flare				
Incinerator	+			+
Other		+ Boiler	+ Boiler	
Material Incinerated, SCFM (Lb./Hr.)	Not Specified	3028		10,050
Auxilliary Fuel Req'd. (excl. pilot)		Yes	Yes	No
Type				
Rate - BTU/hr.				
Device or Stack Height - Ft.	43.75	Not Disclosed ↓	Not Disclosed ↓	85
Installed Cost - Mat'l. & Labor - $				700,000
Installed Cost based on - "year" - dollars				1972
Installed Cost - ¢/lb. of 37% HCHO				.04111
Operating Cost - Annual - $ (1972)				60,000
Operating Cost - ¢/lb. of 37% HCHO				.01233
Efficiency - % - CCR	100			100
Efficiency - % - SERR	100			100

TABLE FS-IV
CATALOG OF EMISSION CONTROL DEVICES
FORMALDEHYDE VIA THE SILVER CATALYST PROCESS

Page 2 of 2

CONDENSERS	
EPA Code No. for plant using	14-8
Flow Diagram Stream I. D.	Δ
Device I. D. No.	FS-6
Controls Emission of	Methanol
Primary Refrigeration Liquid	
Capacity of Refrigeration Unit - Tons	
Gas Rate - SCFM	
Temperature to Condenser - F°	
Temperature out of Condenser - F°	
Liquid Recovered - GPM	Unknown
Non-Condensibles - SCFM	131 lb./hr.
Installed Cost - Mat'l. & Labor - $	3,300
Installed Cost based on - "year" - dollars	1971
Installed Cost - ¢/lb. of 37% HCHO/Yr.	.00220
Operating Cost - Annual - $ (1972)	2,000
Value of Recovered Products - $/Yr	Unknown
Net Operating Cost - Annual - $	
Net Operating Cost - ¢/lb. of 37% HCHO	
Efficiency - % - SE	
Efficiency - % - SERR	

TABLE FS-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980 (2)	Capacity 1980 (2)	Capacity to be Added	Economic Plant Size	Number of New Units
5,914	614	5,300	8,000	9,000	3,700	200	18-19

Note:

(1) All capacities in MM lbs./year.

(2) All capacity estimates based on assumptions that silver catalyzed process does and will account for 77 percent of total U. S. capacity.

TABLE FS-VI
EMISSION SOURCE SUMMARY
TON/TON OF 37% FORMALDEHYDE

Emission	Source			Total
	Absorber Vent	Fractionator Vent	Fugitive Emissions	
Hydrocarbons	.00385	.00015	Negligible	.0040
Particulates	0	0		0
NO_x	0	0		0
SO_x	0	0		0
CO	.0180	0		.0180

TABLE FS-VII
WEIGHTED EMISSION RATES

Chemical Formaldehyde

Process Silver Catalyst

Increased Capacity 3,700 MM Lbs./Year

Pollutant	Emissions, Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factors	Weighted Emissions MM Lbs./Year
Hydrocarbons	.0040	14.8	80	1,184
Particulates	0	0	60	0
NO_x	0	0	40	0
SO_x	0	0	20	0
CO	.0180	65.7	1	67

Significant Emission Index = 1,251

Glycerol (Allyl Chloride)

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I. Introduction

As of January 1971, approximately 300 million pounds per year of synthetic glycerol capacity existed in domestic facilities; in addition, there were approximately 180 million pounds per year of "natural" glycerol capacity. By 1980, installation of approximately 140 mm lbs./yr. of new capacity is envisioned.

The screening effort in this report is limited to the synthetic glycerol category. The specific process studied is the allyl chloride-epichlorohydrin process, and the two questionnaires received are both for this process. Relatively large amounts of chlorine and caustic soda are used, and there is formation of appreciable quantities of chlorinated hydrocarbons - such as propyl chlorides - when this process is employed, but there is basis for its continued use and expansion. The emphasis on this process stems from the fact that epichlorohydrin is formed as an intermediate. Epichlorohydrin is in a favored product position because of its increasing use in materials such as epoxy elastomers.

Other full scale process routes for glycerol exist. Among these are acrolein-allyl alcohol; and allyl alcohol-peracetic acid-glycidol.

Relative to pollution significance, glycerol capacity projections to the year 1980 indicate a weighted SEI (Significant Emissions Index)* of about 700. On this basis, glycerol does not qualify as a petrochemical for in-depth studies.

---

*See Appendix IV for a definition of this term.

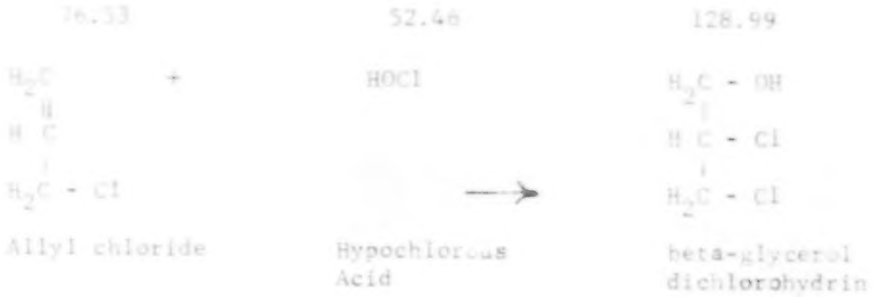
II. Process Descriptions

Simplified flow diagrams of the two processes reported are attached. Please see fold-out Drawing No. R-202 and R-203.

Allyl chloride is transformed into glycerol by means of three successive reaction steps. The first reaction step is from allyl chloride to glycerol dichlorohydrin. The second is from glycerol dichlorohydrin to epichlorohydrin. And the final step is from epichlorohydrin to glycerol.

First reaction step. Glycerol dichlorohydrin is formed by the reaction between chlorine, water and allyl chloride:

70.91		18.02		36.46		52.46
Cl_2	+	HOH	$\longrightarrow$	HCl	+	HOCl
Chlorine		Water (excess)		Hydrochloric Acid		Hypochlorous Acid



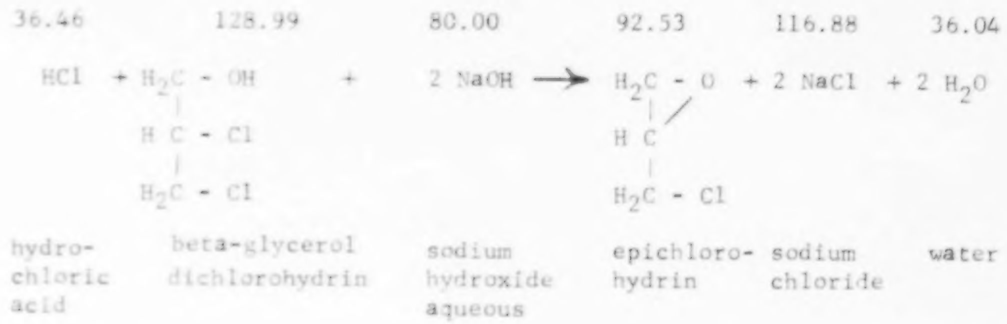
$$\begin{array}{ccccc} 76.53 & & 52.46 & & 128.99 \\ \begin{array}{l} H_2C \\ \ \| \\ H\ C \\ \ | \\ H_2C - Cl \end{array} & + & HOCl & \longrightarrow & \begin{array}{l} H_2C - OH \\ \ | \\ H\ C - Cl \\ \ | \\ H_2C - Cl \end{array} \end{array}$$

(2,3 dichloro, 1-propanol)

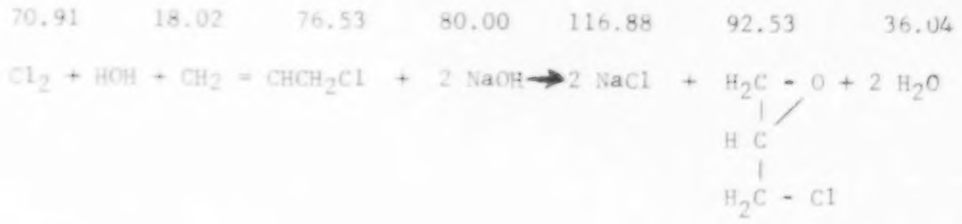
The overall reaction of allyl chloride to glycerol dichlorohydrin, called the "hypochlorination" reaction, may be expressed as:

70.91 18.02	76.53		36.46	128.99
$Cl_2 + HOH +$	$CH_2 = CHCH_2Cl$	$\longrightarrow$	HCl	$+ CH_2OHCHCl\ CH_2Cl$
chlorine water (excess)	Allyl chloride		hydro- chloric acid	beta-glycerol dichlorohydrin (2,3 dichloro, 1-Propanol)

Second reaction step. Epichlorohydrin is formed by the reaction between dilute sodium hydroxide and glycerol dichlorohydrin. The products of the first reaction step (see above) participate as follows in epichlorohydrin formation:


36.46
128.99
80.00
92.53
116.88
36.04
HCl
H2C - OH
H C - Cl
H2C - Cl
2 NaOH
H2C - O
H C
H2C - Cl
+ 2 NaCl
+ 2 H2O
hydrochloric acid
beta-glycerol dichlorohydrin
sodium hydroxide aqueous
epichlorohydrin
sodium chloride
water

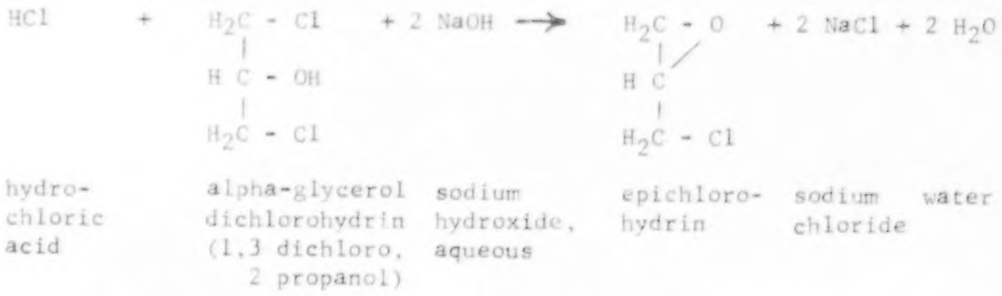
From the above descriptions, it is seen that an overall materials balance can be written for the formation of epichlorohydrin:


70.91
18.02
76.53
80.00
116.88
92.53
36.04
Cl2 + HOH + CH2 = CHCH2Cl + 2 NaOH
2 NaCl
H2C - O + 2 H2O
H C
H2C - Cl

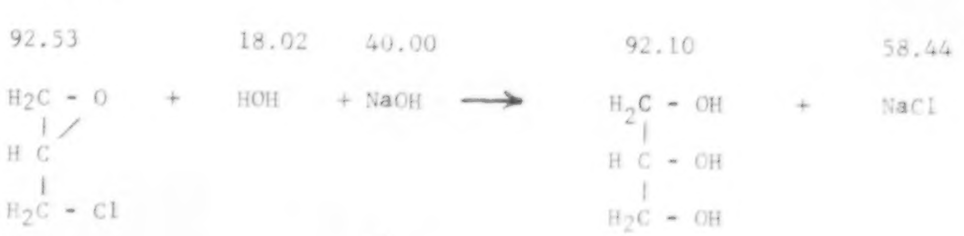
Notes:

1) The net water increase in the above balance does not represent the source of water for the hypochlorination reaction because there is an overbalancing loss of water from this part of the system. This loss occurs through rejection of inorganic salt solutions as waste water.

2) The hypochlorination of allyl chloride also forms 1,3 dichloro, 2-propanol; this material, when reacted with dilute sodium hydroxide, also forms epichlorohydrin:

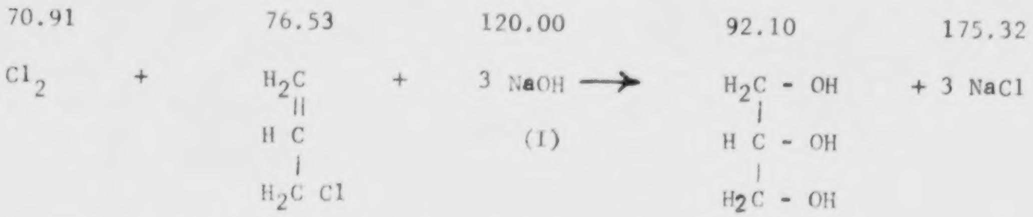

HCl
H2C - Cl
H C - OH
H2C - Cl
+ 2 NaOH
H2C - O
H C
H2C - Cl
+ 2 NaCl + 2 H2O
hydrochloric acid
alpha-glycerol dichlorohydrin (1,3 dichloro, 2 propanol)
sodium hydroxide, aqueous
epichlorohydrin
sodium chloride
water

Third reaction step. Glycerol is formed from the epichlorohydrin obtained in the second reaction step in accordance with the following balance:


92.53
18.02
40.00
92.10
58.44
H2C - O
H C
H2C - Cl
HOH
+ NaOH
H2C - OH
H C - OH
H2C - OH
NaCl

Note that in one of the respondent processes, crude epichlorohydrin is a process feed material. See Drawing No. R-202.

For the entire allyl chloride-to-glycerol process, neglecting side reactions, a simplified balance may be written:



$$\overset{70.91}{Cl_2} + \overset{76.53}{H_2C{=}HC{-}H_2C\,Cl} + \overset{120.00}{3\,NaOH\ (I)} \longrightarrow \overset{92.10}{H_2C{-}OH \,|\, HC{-}OH \,|\, H_2C{-}OH} + \overset{175.32}{3\,NaCl}$$

(I) In the process referenced on Drawing No. R-202, a portion of the total alkali requirement is supplied by $CaCO_3$.

Material balance figures for the two processes reported in the questionnaires are presented in Table I.

The two glycerol questionnaire responses show allyl chloride as a starting material for the glycerol plant operations. It is apparent that this allyl chloride reflects the output of installed plant capacity for reacting propylene with chlorine to make the allyl chloride. Since the resultant glycerol is the reason for making the equivalent quantities of allyl chloride, consideration should be given to the inclusion of allyl chloride process emissions, if glycerol processes should qualify later for in-depth studies.

Further, note should be made of the rapid upswing occurring in epichlorohydrin production, arising from its use in relatively new materials such as epoxy elastomers. This development might result in a future need for review of epichlorohydrin capacity per se, and a subsequent "screening" study for emissions.

An estimated heat balance for the glycerol formation step is shown in Table II.

III. Plant Emissions

A. Continuous Air Emissions

1. Process Vent Streams (see Table III)

Vent streams such as non-condensibles from vacuum process condensing equipment can contain lachrymaters and other potentially undesirable constituents. Principal among this type of constituent, as listed by the questionnaire respondents, are

propyl chlorides
trichloropropane
epichlorohydrin
chlorine
acrolein
dichloropropenes
dichlorohydrins
acetone

Hydrogen is listed in streams B, F and G reported in the 15-1 questionnaire reply. The respondent submitted the following statement as a follow-up to the questionnaire reply:

> "The source of hydrogen in the vent samples taken from streams B, F and G is unknown. The quantity of hydrogen reported would not be expected from process considerations. Before the data could be accepted as typical, additional analyses would be required".

The letter containing the statement quoted above is included in the project file.

Note 1. See Table III heading. Emission figures shown in Table III are for "average amount or composition" as reported in the questionnaire reply submitted by a respondent. The respondent's reply in full is contained in his completed questionnaire under "III, Emissions (composition and flow)".

Note 2. See "Total, Pounds per Stream Hour", stream flow rate. For these two plants, 15-1 and 15-2, flow rates are not characterized as other than continuous by questionnaire respondents.

Note 3. See stream "A", Drawing R-202. Stream "A" is not an emission stream, except when it is vented directly about 10% of the time through vent "B". During direct venting, propyl chlorides are present; however, they are shown flowing at the same rate as that listed in Table III for stream "B", Drawing R-202. Apparently, propyl chlorides are essentially unaffected in passing through Device No. 101, Drawing, R-202. During upsets, chlorine can be vented; such upsets occur 5 to 6 times a year for less than 15 minutes each.

Note 4. See stream "B", Drawing, R-202. In addition to the pollutant factors listed, this stream contains CO_2

1.2 mol. %; air 25.1 mol. %; hydrogen 2.5 mol. %; and water vapor 61.7 mol. %. The water vapor includes the motive steam used for the ejector. Propyl chloride content can double when impure allyl chloride is fed (allyl chloride raw material is listed by the respondent at 97.5 wt. % allyl chloride). During upsets, chlorine can be present, and allyl chloride content can increase up to five times; such upsets occur 5 to 6 times a year for less than 15 minutes each. Production rate during sampling: 50 to 80% of capacity.

Method used to determine (1) composition: mass spectroscopy; (2) flow: vane anemometer. Sampling procedure: evacuated container. Sampling frequency: one spot sample. Confidence level (1) composition: some components may not be accurately identified; (2) flow: "low level of accuracy". Ease of sampling: very difficult. Odor problem: odorous material, chemically identified as propyl and allyl chlorides; detectable at ground level on plant property.

Note 5. See stream "C", Drawing, R-202. Stream "C" is not an emission stream. There is no statement by the respondent similar in principle to the entry on page 6(a) of his questionnaire reply, where he says that stream "A" can vent directly through vent "B". Also, for stream "C", the respondent's entry for item III, 10, Odor Problem, is "not applicable".

Note 6. See stream "D", Drawing, R-202. In addition to the pollutant factors listed, this stream contains misc. non-pollutants 0.24 mol. % and water vapor 99.48 mol. %. "Inerts and organics may vary + 100% of listed value." Production rate during sampling: approximately 50% of capacity. Method used to determine (1) composition: mass spectroscopy; (2) flow: vapor feed meter. Sampling procedure: evacuated cylinder. Two spot samples were obtained; required "climbing column and handling steam sample". Confidence level: "+ 50%". Odor problem: odors detectable beyond plant property; chemical identification trichloropropane and epichlorohydrin. Note that the listings of non-substituted hydrocarbons (less than 0.04 vol. %) are discounted here as unreal and/or inconsequential.

Note 7. See stream "E", Drawing, R-202. Stream "E" is not an emissions stream.

Note 8. See stream "F", Drawing, R-202. In addition to the pollutant factors listed, this stream contains CO_2 64.9 mol. %, misc. non-pollutants 8.1 mol. %; and water vapor 18.2 mol. %. The "organic components are subject to an error of +200% of listed values." Production rate during sampling: approximately 50% of capacity. Method used to determine (1) composition: mass spectroscopy and equilibrium relationships; (2) flow:

based on design CO_2 absorption efficiency. Recirculating water sample analyzed "and the data used to calculate the vent analysis " One spot sample was obtained. No reasonable means to obtain vent vapor sample. Odor problem: odors detectable beyond plant property and affirmative answer relative to community complaint; chemical identification isopropyl chloride and trichloropropane.

Note 9. See stream "G", Drawing R-202. This stream is stated to contain hydrogen 18.6 mol. % and water vapor 79.0 mol. %. Confidence level + 50%. Production rate during sampling: approximately 50% of capacity.

The stream "includes 5 vacuum jets and 4 accumulator vents". The largest jet was sampled via evacuated cylinder and its flow measured by vane anemometer. The smaller jets are estimated to total 5 to 10% of the large jet emissions. One spot sample was taken and analyzed by mass spectroscopy. Odor was detectable at ground level on plant property. If the stream analysis is qualitatively correct, this odor is presumably one or more components from the group propylene, butylene, acetone, and ethane. It will be observed that the average molecular weight of the stream is a little over one-half that of air.

Subsequent to the questionnaire's return, the respondent submitted a letter (on file) indicating that the analytical data are possibly atypical with respect to hydrogen.

Note 10. See stream "A" Drawing, R-203. Chlorine average composition is 0.7 mol. %; range is 0 - 3 mol. %. Epichlorohydrin average composition is 0.02 mol. %; range is 0 - 0.04 mol. %. Production rate corresponding to estimated stream "A" flow rate is not reported. Stream "A" flow rate estimated from chlorine feed rate (no sampling). Composition estimated from inerts composition in chlorine. (For sampling) would use vacuum sample bottle. (For analytical procedure) would use flame VPC for organic constituents.

Confidence level for composition is "fair"; for (flow) rate is "high". Ease of sampling: (Sampling would be) difficult. Odor is detectable at ground level on plant property; odorous material chemically identified as chlorine.

Note 11. See stream "B" - Propyl chlorides average composition is 0.25 mol. %; range is 0.15 - 0.75 mol. %. Epichlorohydrin average composition is 0.025 mol. %; range is 0.015 - 0.050 mol. %. Production rate during sampling "14,000 lbs./hr. crude EPI". Method used to determine (1) composition: flame VPC; (2) flow: air anemometer. Sampling procedure: "Vacuum bottle". Analytical procedure: flame VPC. Sampling frequency: "Infrequently". Confidence level (1) composition: high; (2) flow: moderate. Ease of sampling: moderate. Odor problem: No problems.

Note 12. See stream "C". (This stream was) never sampled. Composition variation, composition and flow are estimated. There is no sampling or analytical procedure. Confidence level (1) Composition: relatively high; (2) flow: rather questionable. Ease of sampling, rather difficult. Odor problem: No problems.

Note 13. See stream "D". Same notes as under Note 12, except ease of sampling relatively simple.

Note 14. See stream "E". Production rate during sampling 380,000 lbs./day glycerol. Composition by VPC; flow estimated. Sampling by vacuum bottle; analytical procedure, VPC. Sampling frequency, "Once". Ease of sampling, "Very difficult; poor access to sampling point". Odor problem: No problems.

Note 15. See stream "F". Stream F never sampled. Composition and flow estimated. Ease of sampling, "Possible". Odor problem: No problems.

Note 16. See stream "G". Same notes as under Note 15, except ease of sampling, difficult.

Note 17. See stream "H". Same notes as under Note 15, except ease of sampling, no entry.

Note 18. See stream "I". Same notes as under Note 15, except ease of sampling, no entry.

Note 19. See stream "J". Same notes as under Note 15, except ease of sampling, no entry.

Note 20. See stream "K". Same notes as under Note 15, except ease of sampling, "relatively simple".

III. Plant Emissions

A. Continuous Air Emissions (Cont'd.)

2. Storage Losses

The following materials are stored without vapor conservation:

Epichlorohydrin
Toluene
Glycerol & related

Materials stored with a "pad" are reported as follows:

Acetone
Various mixtures containing items such as glycerol, acetone and p-dioxane dimethanols.

The contributions to emissions relative to the above storage categories have no significant effect on the SEI.

B. Intermittent Air Emissions

One respondent reports nothing of consequence. The other provides no comment. There is not any indication that intermittent emissions associated with start-ups or emergencies would have a significant effect on the SEI. If allyl chloride production (from chlorine and propylene) were included (at a future time) within the scope of the glycerol production category, then chlorine could be an emergency vent.

C. Continuous Liquid Wastes

One respondent indicates 1,200 GPM of waste water, with 100% treatment by primary and secondary in-plant treatment. The other says "1,500 GPM aqueous waste, most of this to disposal well".

Neutralization reactions occur in the process. These (net) reactions are between caustic soda and hydrochloric acid, or calcium carbonate and hydrochloric acid. Please see under Process Description for specific reactions. The sodium chloride solutions and calcium chloride solutions leaving the process as a result of these neutralization reactions are considered part of the waste water stream.

D. Intermittent Liquid Wastes

There is no indication of significant contribution from such sources. And, barring double jeopardy, the influence of intermittent liquid waste factors would presumably be damped out by the realtively large flow of continuous liquid wastes.

E. Solid Wastes

There are no discreet solid wastes.

F. Odors

Odors reported by the two questionnaire respondents are chemically identified by them according to the following list of constituents:

Propyl chlorides, normal and iso-
Allyl chloride
Trichloropropane
Epichlorohydrin
Chlorine

There are other odorous materials in some of the vent streams; for example,

Acrolein
Dichloropropenes
Dichlorohydrins
Acetone
Hydrocarbons, non-substituted

Some of the entries in the above lists are lachrymators. And the maximum allowable concentration in air can range as low as 0.5 parts per million for an item such as acrolein

G. Fugitive Emissions

One respondent leaves this category blank (Section VIII, Other Emissions); the other indicates that there are the usual contributions from leaks, sampling, gauge glass blowdowns, and equipment purging for maintenance. The magnitude of these losses is not known.

Emergency release from pressure saftey valves, rupture discs, etc., is excluded from consideration here. Further, it is assumed that the contents of storage tanks listed as "padded" do not contribute to "Fugitive Emissions". On this basis, there remains for review the category of storage tanks without pads.

Atmospheric storage tanks listed by the respondents as being unpadded or not requiring a method of vapor conservation are stated to contain one or more of the following materials:

Glycerol
Polyglycerols
NaCl
Water
Toluene
Epichlorohydrin

The maximum storage temperature is at the high end of the ambient range, say 130 °F (54 °C). The materials in the list above have relatively low vapor pressures, except for toluene and epichlorohydrin which exhibit vapor pressures of approximately 2 PSIA at 130 °F. For atmospheric storage of these items, vapor pressure = partial pressure. Thus, a fugitive emission could arise during toluene or epichlorohydrin tank filling. For epichlorohydrin, the order-of-magnitude of such emission could be as high as 50 lbs./hr. at a vent concentration of about 14 volume per cent in air.

IV. Emission Control

Emission control devices indicated by the questionnaire respondents are listed in Table IV.

Since the SEI for glycerol is low and not within the in-depth study bounds, the devices indicated are presumed adequate.

It should be noted that there are lachrymator components in some of the emission streams.

The efficiencies of the control devices as determined by the definition included in Table IV show extreme values running from "zero" to over 99% efficiency. The explanation of this variation from one stream component to another is found by examining the objective of each emission control device.

The objective of emission control device 15-1-101 is to scrub out the CO_2 in the entering vapor stream. The use of a relatively mild alkaline solution achieves this objective. Components such as propyl chloride which encounter this same alkaline scrubbing solution (along with the CO_2) are essentially unaffected, however. Thus, with the component flow leaving the device equal to the component flow entering (expressed in consistent units such as pounds per hour), the efficiency calculated equates to zero.

Referring to Table IV, it will be noted that Emission Control Device 15-1-102 shows a behavior akin to that of device 15-1-101, except that the efficiency of the control means for the epichlorohydrin is 52%. In this instance, the epichlorohydrin exhibits significant reactivity with the alkaline scrubbing medium. This behavior reflects the relative ease with which the (strained) oxygen-carbon bonds are broken under the condition existing in the scrubber.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time. Although the projected growth rate of glycerol capacity is significant, the emission data indicate that the quantity of pollutants emitted to the atmosphere is less, on a weighted basis, than from many of the other processes that are currently being surveyed.

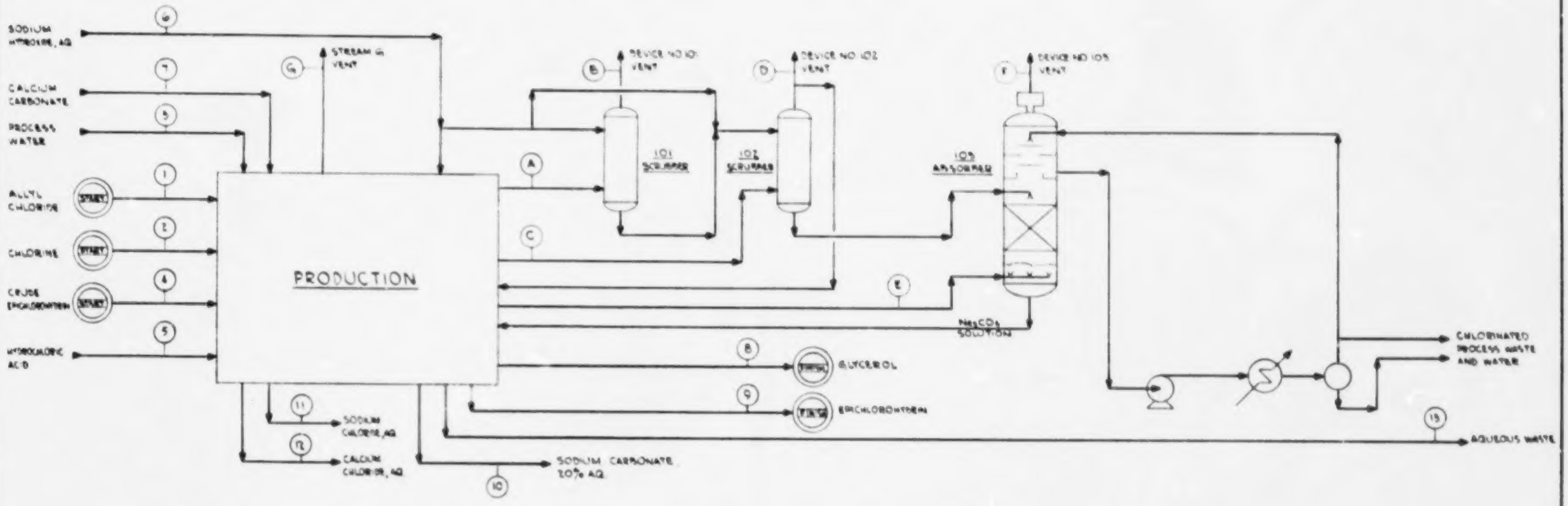
The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emissions of pollutants. See Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index (SEI) of 700 has been calculated (Table VI). This is substantially less than SEI's that are anticipated for other processes in the study.

VI. Glycerol Producers (Domestic)

Company	Location	Capacity MM Lbs./Year
Alba Manufacturing	Aurora, Ill.	*
Armour - Dial	Montgomery, Ill.	*
Ashland Chemical	Peoria, Ill.	*
Colgate-Palmolive	Berkeley, Calif.	*
	Jeffersonville, Ind.	*
	Jersey City, N. J.	*
	Kansas City, Kansas	*
Dow Chemical	Freeport, Texas	120
Emery Industries	Cincinnati, Ohio	*
	Los Angeles, Calif.	*
FMC Corporation	Bayport, Texas	40
Kewanee Oil, Harshaw Chem. Div.	Gloucester City, N. J.	*
Kraftco Corporation Humko Products Div.	Memphis, Tenn.	*
Lever Brothers	Baltimore, Md.	*
	Hammond, Ind.	*
	Los Angeles, Calif.	*
Murro Chemical	Portsmouth, Va.	*
Pacific Soap	Los Angeles, Calif.	*
Procter & Gamble	Baltimore, Md.	*
	Chicago, Ill.	*
	Dallas, Texas	*
	Ivorydale, Ohio	*
	Long Beach, Calif.	*
	Port Ivory, Staten Island, N. Y.	*
Purex Corporation	Bristol, Pa.	*
Shell Oil Co. Shell Chem. Co.	Houston, Texas	125
	Norco, La.	50
Swift & Co. Swift Chem. Co.	Hammond, Ind.	*
Union Camp. Corp. Harchem Div.	Dover, Ohio	*

*"Natural" glycerine sources, capacities not listed.


SODIUM HYDROXIDE, AQ
CALCIUM CARBONATE
PROCESS WATER
ALLYL CHLORIDE
CHLORINE
CRUDE EPICHLOROHYDRIN
HYDROCHLORIC ACID
START
6
7
3
1
2
4
5
G
STREAM G VENT
PRODUCTION
A
C
B
DEVICE NO 101 VENT
101 SCRUBBER
D
DEVICE NO 102 VENT
102 SCRUBBER
F
DEVICE NO 103 VENT
103 ABSORBER
E
Na_2CO_3 SOLUTION
8
GLYCEROL
9
EPICHLOROHYDRIN
FINISH
11
SODIUM CHLORIDE, AQ
12
CALCIUM CHLORIDE, AQ
10
SODIUM CARBONATE 20% AQ
13
AQUEOUS WASTE
CHLORINATED PROCESS WASTE AND WATER

NOTES

1 CIRCLED NUMBERS (①) REFER TO MATERIAL BALANCE STREAMS
2 CIRCLED LETTERS (Ⓐ) REFER TO ATMOSPHERIC VENTS AS DETAILED IN TABLE II.

SCALE	NONE	DATE
DRAWN BY	E. ANDERSON	[illegible]
CHECKED BY		[illegible]
CATALYTIC APPROVAL		
CLIENT APPROVAL		[illegible]

THE
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0295

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT, PHILADELPHIA, PENNA. [illegible]

FIGURE 6-1
SIMPLIFIED FLOW DIAGRAM
FOR
GLYCEROL PRODUCTION (13-1)

PROJECT NO. 62030
420
DWG. NO. R-202
REV. NO. A

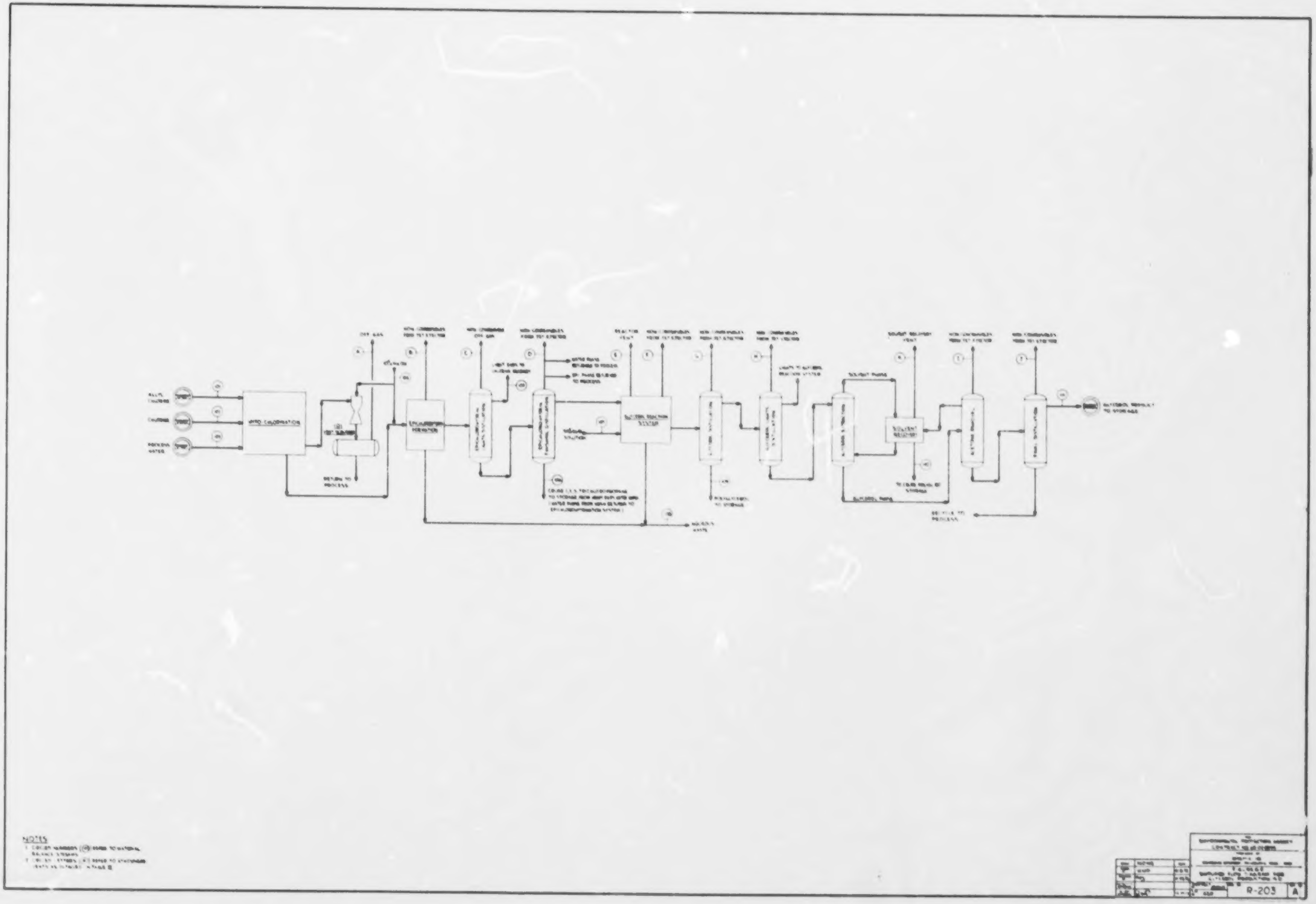
OFF GAS
NOTES
R-203
A

TABLE G-1
MATERIAL BALANCE FOR GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE AS RAW MATERIALS

Page 1 of 3

Company							
Location and/or EPA Coded Number		15-1					
Nameplate capacity in short tons of glycerol product per year		47,500					
Simplified flow diagram stream designation	1	2	3	4	5	6	7
Description of Stream	Allyl Chloride Feed	Chlorine Feed	Process Water Feed	Crude epi-chlorohydrin Feed	Hydro-chloric Acid	Sodium Hydroxide Aqueous	Calcium Carbonate
Component							
Allyl chloride	1.2316						
Other organic chlorides (presumed other monochloroprenes)	0.03158						
Chlorine		1.1567					
Chlorine inerts		0.00116					
Sodium hydroxide							
Sodium chloride							
Water			Not given	0.01158	0.05158		
Sodium hydroxide in aqueous solution						1.4211	
Calcium carbonate							0.7658
Calcium carbonate inerts							0.0237
Hydrogen chloride					0.02211		
Epichlorohydrin				0.5095			
Epichlorohydrin heavy ends				0.04632			
Epichlorohydrin light ends				0.01158			
Glycerol							
ISO-propyl and N-propyl chlorides							
Acrolein							
2, 3 dichloropropene							
1, 2, 3 trichloropropane							
Bis-dichloropropyl ether							
Glycerol dichlorohydrin							
Polyglycerol mixture							
P-dioxane dimethanols							
2-2 dimethyl, 1,3 dioxolane, 4-methyol							
Acetone							
Sodium carbonate							
Calcium chloride							
Waste water							
Total, tons per ton of glycerol capacity	1.2632	1.1579	Not given	0.5790	0.07369	1.4211	0.7895

TABLE G-I
MATERIAL BALANCE FOR GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE AS RAW MATERIALS

Page 2 of 3

Company						
Location and/or EPA Coded Number		15-1				
Nameplate capacity in short tons of glycerol product per year		47,500				
Simplified flow diagram stream designation	8	9	10	11	12	13
Description of Stream	Glycerol Product	Epichloro-hydrin Product	Sodium Carbonate 20% Aqueous	Sodium Chloride, Aqueous	Calcium Chloride, Aqueous	Aqueous Waste
Component						
Allyl chloride						
Other organic chlorides (presumed other monochloropropenes)						
Chlorine						
Chlorine inerts						
Sodium hydroxide						
Sodium chloride				2.053		
Water	0.003		0.04211	Present	Present	
Sodium hydroxide in aqueous solution						
Calcium carbonate						
Calcium carbonate inerts						
Hydrogen chloride						
Epichlorohydrin		0.7309				
Epichlorohydrin heavy ends						
Epichlorohydrin light ends		0.00589				
Glycerol	0.997					
ISO-propyl and N-propyl chlorides						
Acrolein						
2, 3 dichloropropene						
1, 2, 3 trichloropropane						
Bis-dichloropropyl ether						
Glycerol dichlorohydrin						
Polyglycerol mixture						
P-dioxane dimethanols						
2-2 dimethyl, 1,3 dioxolane, 4-methyol						
Acetone						
Sodium carbonate			0.01053			
Calcium chloride					0.8737	
Waste water						
Total, tons per ton of glycerol capacity	1.000	0.7368	0.05264	2.053+ Water	0.8737+ Water	(1,200 GPM)

TABLE G-1
MATERIAL BALANCE FOR GLYCEROL PLANTS USING EPICHLOROHYDRIN
AND/OR ALLYL CHLORIDE AS RAW MATERIALS

Page 3 of 3

Company											
Location and/or EPA Coded Number			15-2								
Nameplate capacity in short tons of glycerol product per year			55,000								
Simplified flow diagram stream designation	101	102	103	104	105	106	107	108	109	110	111
Description of Stream	Allyl Chlorine Feed	Chlorine Feed	Process Water Feed*	Caustic Feed, 10 wt. %	EPI Lights	1, 2, 3 Tri-Chloro-propane	Caustic Feed, 50 wt. %	Aqueous Waste	Poly-glycerol	Polyol 80	Glycerol Product
Component											
Allyl chloride	1.0925				0.005236						
Other organic chlorides (presumed other monochloroprenes)	0.01664										
Chlorine		0.98023									
Chlorine inerts		0.05160									
Sodium hydroxide				1.309			0.5818				
Sodium chloride				1.964							
Water			0.2355	9.818			0.5818				0.002
Sodium hydroxide in aqueous solution											
Calcium carbonate											
Calcium carbonate inerts											
Hydrogen chloride											
Epichlorohydrin					0.0007273	0.001455					
Epichlorohydrin heavy ends											
Epichlorohydrin light ends											
Glycerol										0.02727	0.998
ISO-propyl and N-propyl chlorides					0.007127						
Acrolein					0.0007273						
2, 3 dichloropropene					0.0007273						
1, 2, 3 trichloropropane						0.1164					
Bis-dichloropropyl ether						0.01745					
Glycerol dichlorohydrin						0.01018					
Polyglycerol mixture									0.08182		
P-dioxane dimethanols										0.006909	
2-2 dimethyl, 1, 3 dioxolane, 4-methyol										0.001455	
Acetone										0.0007273	
Sodium carbonate											
Calcium chloride											
Waste water											
Total, tons per tons of glycerol capacity	1.109	1.0318	0.2355	13.091	0.01455	0.1455	1.1636	(1,500 GPM)	0.08182	0.03636	1.000
			*Amount Required for Reaction Only								

TABLE G-II
GLYCEROL PLANTS
USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE
GROSS HEAT BALANCE (EST'D.)
GLYCEROL REACTION STEP

Heat Out

Heat of vaporization of water, vacuum evaporation		250	BTU/LB. Glycerol Formed
Losses, sensible heat effects, heats of solution, etc.		18	
	Total	268	

Heat In

Exothermic heat of reaction		268	BTU/LB. Glycerol Formed
	Total	268	

TABLE G-III
NATIONAL ATMOSPHERIC EMISSIONS INVENTORY
FOR
GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE (NOTE 1)

Company							
Location and/or EPA Coded Number		15-1					
Date on-stream							
"Nameplate" capacity in short tons of glycerol product per year		47,500					
Approximate average production rate, tons glycerol per year							
Seasonal variation in production rate, percent of nameplate capacity		None					
Simplified flow							
Description diagram stream designation	A	B	C	D	E	F	G
Allyl chloride		Incl'd in propyl chlorides				Incl'd in propyl chlorides	
chlorine							
Iso-propyl alcohol				0.001665		0.0004283	
Iso-and n-propyl chlorides		0.02631				0.001791	
1, 2, 3 trichloropropane				0.003269		0.001681	
Acrolein							
2, 3 dichloropropene							
Epichlorohydrin				0.001539			
Acetone				0.005151			0.001840
Water							
Air							
Hydrocarbon, non-substituted (for example, ethane, propene, butene)		0.008238				0.003622	0.01026
CO_2							
2, 3 dichlorohydrin							
	Note 3	Note 4	Note 5	Note 6	Note 7	Note 8	Note 9
Total, Tons per ton of glycerol capacity (330 operating days/Cy assumed)		0.03455		0.01162		0.007522	0.0121
Total, pounds per stream hour (note 2)		414		140		91	146
Total, SCFM at 60° F and 14.7 PSIA		300		2,100		54	400
Temperature, °F		250		220 - 240		150	250
Temperature, °C		121		104 - 116		66	121
Pressure, PSIG		Atm		3 - 7		Atm	Atm
Sampling location		Scrubber Vent					
Date or frequency of sampling		One spot sample					
Type of Analysis		Mass spectro.					
Odor presence		C_3 Chlorides					
Vent stacks							
Number		1		1		1	5 vacuum jets/ 4 accumulator vents
Height, Feet		60		100		100	50/30
Diameter, Inches		8		8		10	4/2
Temperature, Stack exit, °F		250		230		150	250/200
°C		121		110		66	121/93
Emission Control Devices							
Type		Scrubber		Scrubber		Scrubber	
Catalog Identification No.; see Table IV		15-1-101		15-1-102		15-1-103	
Total emissions expressed as tons/ton glycerol capacity							
Hydrocarbon		0.03455		0.01162		0.007522	0.0121
Particulate, Aerosol		None		None		None	None
[illegible]		None		None		None	None
[illegible]		None		None		None	None
		None		None		None	None

See pages 1-3 through 1-6 for explanation of notes.

TABLE C-III
NATIONAL ATMOSPHERIC EMISSIONS INVENTORY
FOR
GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE (NOTE 1)

Page 2 of 4

Company	
Location and/or EPA Coded Number	15-2
Date on-stream	
"Nameplate" capacity in short tons of glycerol product per year	55,000
Approximate average production rate, tons glycerol per year	
Seasonal variation in production rate, percent of nameplate capacity	None
Simplified flow	

Description diagram stream designation	A Hypochlorination vent	B Hydrolizer vent	C EPI Lights dist'n vent	D EPI finishing dist'n vent	E Glycerol reactor vent
Allyl chloride			0.0001056		
chlorine	0.0009467				
Iso-propyl alcohol					
Iso-and n-propyl chlorides	0.00001527	0.0001717	0.0001894		
1, 2, 3 trichloropropane					
Acrolein			0.00004284		Trace
2, 3 dichloropropene			0.000009720	0.000002882	
Epichlorohydrin	0.00003627	0.00002015	0.00001332	0.0001355	Trace
Acetone					
Water	0.003165	0.001425		0.0001499	Majority
Air	0.04982	0.02286			
Hydrocarbon, non-substituted (for example, ethane, propene, butene)					
CO_2					Trace
2, 3 dichlorohydrin					
	Note 10	Note 11	Note 12	Note 13	Note 14
Total, tons per ton of glycerol capacity (330 operating days/cy assumed)	0.0540	0.02448	0.00036	0.000288	0.000205
Total, pounds per stream hour (note 2)	750	340	5	4	2.85
Total, SCFM at 60° F and 14.7 PSIA	167.4	76.4			1
Temperature, °F	86 - 122	69 - 104	Amb.	86 - 104	104
Temperature, °C	30 - 50	20 - 40	Amb.	30 - 40	40
Pressure, PSIG	0 - 3	0 - 1	0 - 1	0 - 1	Atm
Sampling location	None	Not Given	None	None	Not Given
Date or frequency of sampling	None	Infrequent	None	None	Once
Type of analysis	None	Flame VPC	None	None	VPC
Odor presence	Chlorine	None	None	None	None
Vent stacks					
Number	1	1	1	1	1
Height, Feet	70	42	55	58	30
Diameter, Inches	8	4	2	2	10
Temperature, Stack exit, °F	113	104	Amb.	104	104
°C	45	40	Amb.	40	40
Emission Control Devices					
Type	Jet Fume Scrubber				
Catalog Identification No. - see Table IV	Glycerol 15-2 101				
Total emissions expressed as tons/ton glycerol capacity					
Hydrocarbon	0.001015, incl. chlorine	0.000195	0.00036	0.000138	None
Particulate, Aerosol	None	None	None	None	None
NO_x	None	None	None	None	None
SO_x	None	None	None	None	None
CO	None	None	None	None	None

See pages [illegible] through [illegible] for explanation of notes.

TABLE G-III
NATIONAL ATMOSPHERIC EMISSIONS INVENTORY
FOR
GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE (NOTE 1)

Company			
Location and/or EPA Coded Number	15-2		
Date on-stream			
"Nameplate" capacity in short tons of glycerol product per year	55,000		
Approximate average production rate, tons glycerol per year			
Seasonal variation in production rate, percent of nameplate capacity	None		
Simplified flow Description diagram stream designation	F Glycerol Evap Vent	G Glycerol Dist'n Vent	H Glycerol Light Dist'n Vent
Allyl chloride			
chlorine			
Iso-propyl alcohol			
Iso-and n-propyl chlorides			
1, 2, 3, trichloropropane			
Acrolein			
2, 3 dichloropropene			
Epichlorohydrin			
Acetone			
Water	100%	100%	100%
Air			
Hydrocarbon, non-substituted (for example, ethane, propene, butene)			
CO_2			
2, 3 dichlorohydrin			
Total, tons per ton of glycerol capacity	Note 15	Note 16	Note 17
(330 operating days/yr assumed)	0.0216	Unknown	0.03600
Total, pounds per stream hour (note 2)	300	"Very Small"	500
Total, SCFM at 60°F and 14.7 PSIA	105.3		175.5
Temperature, °F	212	95 - 100	212
Temperature, °C	100	35 - 38	100
Pressure, PSIG	0 - 3	Atm.	5
Sampling Location	None	None	None
Date or frequency of sampling	None	None	None
Type of analysis	None	None	None
Odor presence	None	None	None
Vent stacks			
Number	1	No information supplied	
Height, Feet	49		
Diameter, Inches	1		
Temperature, Stack exit, °F	104		
°C	40		
Emission Control Devices			
Type			
Catalog Identification No., See Table IV			
Total emissions expressed as tons/ton glycerol capacity			
Hydrocarbon	None	None	None
Particulate, aerosol	None	None	None
NO_x	None	None	None
SO_x	None	None	None
CO	None	None	None

See pages G-5 through G-8 for explanation of notes.

TABLE G-III
NATIONAL ATMOSPHERIC EMISSIONS INVENTORY
FOR
GLYCEROL PLANTS USING EPICHLOROHYDRIN AND/OR ALLYL CHLORIDE (NOTE 1)

Page 4 of 4

Company			
Location and/or EPA Coded Number			
Date on-stream	15-2		
"Nameplate" capacity in short tons of glycerol product per year			
Approximate average production rate, tons glycerol per year	55,000		
Seasonal variation in production rate, percent of nameplate capacity			
Simplified flow			
Description diagram stream designation	I Acetone Removal Vent	J Final Dist'n. Vent	K Solvent Recovery Vent
Allyl chloride			
chlorine			
Iso-propyl alcohol			
Iso-and n-propyl chlorides			
1, 2, 3 trichloropropane			
Acrolein			
2, 3 dichloropropene			
Epichlorohydrin			
Acetone			
Water	Trace		
Air	≈ 100%	100%	100%
Hydrocarbon, non-substituted (for example, ethane, propene, butene)			
CO_2			
2, 3 dichlorohydrin			
Total, tons per ton of glycerol capacity	Note 18	Note 19	Note 20
(330 operating days/cy assumed)	0.07200	0.0288	0.00144
Total, pounds per stream hour (note 2)	1,000	400	20
Total, SCFM at 60° F and 14.7 PSIA	350.9	140.4	2.2
Temperature, °F	212	212	95 - 104
Temperature, °C	100	100	35 - 40
Pressure, PSIG	0 - 5	0 - 5	Atm.
Sampling Location	None	None	None
Date or frequency of sampling	None	None	None
Type of analysis	None	None	None
Odor presence	None	None	None
Vent stacks		No Information Supplied	
Number			
Height, Feet			
Diameter, Inches			
Temperature, Stack exit, °F			
°C			
Emission Control Devices			
Type			
Catalog Identification No., See Table IV			
Total emissions expressed as tons/ton glycerol capacity			
Hydrocarbon	Trace	None	None
Particulate, aerosol	None	None	None
NO_x	None	None	None
SO_x	None	None	None
CO	None	None	None

See Pages [illegible] through [illegible] for explanation of notes.

TABLE G-IV
EMISSION CONTROL MEANS (1972)
GLYCEROL VIA ALLYL CHLORIDE-EPICHLOROHYDRIN

Company				
Location of Plant and/or EPA Coded Number		15-1		15-2
Type of Emission Control Means & Manufacturer	Packed Scrubber Pioneer Industrial	Packed Scrubber Pioneer Industrial	Scrubber Trays & Packing Pioneer Industrial	Jet Fume Scrubber S & F
Emission Device Identification No.	15-1 - 101	15-1 - 102	15-1 - 103	15-2 - 101
Device to Control Emission of	CO_2 & Chlorinated Organics	CO_2 & Organics	CO_2 & Organics	Chlorine & Chlorinated Organics
Jets				
Type	Steam	None	None	Fume Scrubber
Number	One ?			One
Packing				
Type	Shaped Bodies	Rings	Units	
Material	Polypropylene	Steel	Polypropylene	
Size, Inches	3	3	3	
Nominal Height, Feet of Packed Section	1[illegible]	30	40	
Trays				
Type			Distribution	
Material			?	
Number			?	
Temperature, °C. (°F)	66 (150)	110 (230)	66 (150)	50 (122)
Pressure	Sl. Vacuum	5 PSIG	Sl. Positive	0 - 3 PSIG
Liquid Contacting Medium				
Rate, USGPM, through Contacting Medium	40	70	80 each for trays & packing	
Composition, Nominal (when fresh)	NaOH Solution	NaOH Solution		
Make-up rate	2,000 Lbs./Hr. NaOH (100% basis)	40 GPM fresh; 40 GPM from 15-1 - 101	85 GPM from 15-1 - 102	
Net Flow Leaving, USGPM		To 15-1 - 103, 80 GPM		
Vapor **Rate**, SCFM (Lbs./Hr.) into device	500	2,000	500	
leaving device	150 to Jet		50	
Column Height, T/T, Feet	30	50	65	
Column Diameter, Inches	24	48	36	
Efficiency of Control Means	CO_2 99.2: **Propyl** Chloride Eff. = 0	CO_2 99.0; **Epi-** chlorohydrin 52	CO_2 92.6	
Pump H.P.	1/2	15	20	
Steam Rate, lbs./Hr.	1,200	No Steam		
Cost Data				
Installed Cost, Material & Labor, Direct	$20,000	$50,000	$75,000	$15,000
Installed Cost, Dollars per Ton Glycerol Capacity/Yr.	$0.4211	$1.053	$1.58	$0.2727
Year of Installed Cost Accounting	1960	1957	1957	1969
Operating Cost, Annual (1972)	$20,000	$3,000	$71,000	Maint. $1,000, Credit $1,000
Operating Cost, Dollars per ton Glycerol Capacity/Yr.	$0.4211	$0.0632	$1.50	Zero
Accounting Credits	$NaCO_3$ Recovered offsets NaOH make-up (NaOH 2,000 Lbs./Hr.)	Na_2CO_3 Recovered offsets NaOH make-up (NaOH 7,000 Lbs./Hr.) Steam Recovery Credit is $15,000	("Other Disposal" entry = $50,000 per year)	Operating Costs listed are balanced by credits

TABLE C-V

NUMBER OF NEW PLANTS BY 1980

Chemical	Process	Current Capacity MM Lbs./Yr.	Marginal Capacity MM Lbs./Yr.	1971 Capacity Extant as of 1980 MM Lbs./Yr.	Consumer Demand 1980 MM Lbs./Yr.	Projected Capacity 1980 MM Lbs./Yr.	New Capacity by 1980 MM Lbs./Yr	New Units by 1980*
Glycerol	Allyl chloride-epichlorohydrin	245	0	245		380	135	1
	Acrolein-allyl alcohol	50	0	50		50		
	Allyl alcohol-peracetic acid-glycidol	40	40	0				
	"Natural"	160	[illegible]	160		160		
	Total	495	40	455	470	590	135	1

*Basis new unit designed for economic rate = 135 MM Lbs./Yr.; 1971 units are about 100 MM Lbs./Yr. capacity each

**Assume marginal drop-outs are balanced off by closer approach to full capacity by surviving plants.

TABLE G-VI
WEIGHTED EMISSION RATES

Chemical: Glycerol

Process: Allyl chloride -
epichlorohydrin**

Est. New Capacity as of 1980: 135 MM LBS./YR.

Pollutants	Emissions Lb. per Lb. Glycerol Capacity	Est. New Emissions as of 1980, MM LBS./YR.	Weighting Factors	Weighted Emissions as Index Units
Hydrocarbons*	0.06579 ***	8.88	80	700
Particulate	None	None	60	0
NO_x	None	None	40	0
SO_x	None	None	20	0
CO	None	None	1	0
		Grand Total, Weighted Pollutant Emission Index	=	700

---

*Including organic compounds containing oxygen and/or chlorine, as well as hydrogen and carbon.

**Other processes are not in questionnaire respondent status (as of November, 1972); see Table V.

***See Table VII for component sources of this cumulative figure.

TABLE G-VII

COMPONENT EMISSION RATIOS*

	Stream from Table III, Process 15-1**				
Pollutants***	B	D	F	G	Total
Hydrocarbons	0.03455	0.01162	0.007522	0.0121	0.06579
Particulate	None	None	None	None	None
NO_x	None	None	None	None	None
SO_x	None	None	None	None	None
CO	None	None	None	None	None
Total	0.03455	0.01162	0.007522	0.0121	0.06579

*Used in cumulative total form in Table VI.

**Process 15-1 was selected (rather than Process 15-2) as representing the more conservative approach for SEI calculation purposes.

***Units are tons of pollutants per ton of glycerol capacity.

Hydrogen Cyanide (Andrussow)

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I. Introduction

According to information in SRI's Chemical Economics Handbook, (viii), probably considerably less than 10% of the hydrogen cyanide produced in the United States today is available in the merchant market. Most producers have integral facilities for captive use, and ordinarily maintain relatively small quantities in intermediate storage. Discrepancies in published figures for both capacity and consumption apparently stem from this difficult-to-assess captive use. Although substantial quantities of hydrogen cyanide were going into the production of acetylene derived acrylonitrile, this use has been eliminated by the propylene process, which actually results in production of hydrogen cyanide instead. In the early 1960's, over 50% of the HCN produced was consumed in the making of acrylonitrile and since this outlet no longer exists, and anticipated hydrogen cyanide consumption increases for nitrilotriacetate have not materialized, gains in other areas have been barely enough to make up for the loss. With the trends predicated in the January, 1971 CEH report, estimated breakdown for consumption of hydrogen cyanide is as shown here:

Acetone Cyanohydrin (for methacrylate polymers)	45%
Adiponitrile (HCN derivation only) for Nylon 6,6	33%
Chelating agents	11%
Sodium Cyanide	5%
Other	6%

Emissions from the direct production of hydrogen cyanide from methane, ammonia and air are very low, in keeping with the fact that the product is highly toxic. Normal sample pot vents result in low-level hydrogen cyanide emission, and air dilution and dissipation by release from high stacks provides the means for safe disposal. Flaring of process off-gas and certain other process equipment vent streams results in NO_x formation which is negligible except at times of start-up or emergency.

The advent of an acrylonitrile process that actually produces by-product hydrogen cyanide instead of using it as raw material has resulted in excess capacity and leveling off of consumption. Some direct process hydrogen cyanide will undoubtedly remain on-stream due to captive market predominance but new capacity will be provided via the by-product route in an expanding market for acrylonitrile. No new direct process capacity is anticipated and for that reason, emissions from this process will likely decrease as plants become obsolete.

II. Process Description

The direct route used in this country for producing hydrogen cyanide from methane, ammonia and air is based on the Andrussow process with certain modifications initiated by Degussa, Montecatini, B. F. Goodrich and others. Figure I presents a simplified block flow diagram. (i, ii, iii, iv, v, vi, ix) With the air preheated, purified reactants are passed over a precious metal gauze or impregnated catalyst at one atmosphere and 1000 to 1200° C (1830 to 2200° F). The catalyst promotes the complex oxidation reaction, which is carried out beyond the flammable limits on the fuel-rich side (see Table I for the significant reactions involved). Although the production of hydrogen cyanide directly from methane and ammonia would be endothermic, the overall reaction involving oxidation is highly exothermic, and to minimize non-selective decomposition products, the reactor effluent must quickly be cooled in a waste heat boiler. The catalyst, feed gas purity and ratios, contact time, materials of construction, reactor and quench zone geometry and other factors all have an influence on conversion, yield and productivity. Table II attached provides typical weight balance data, here based on an air:methane:ammonia mol. ratio of 6:1:0.9. Conditions are chosen so that reactions III and IV (Table I), giving rise to carbon dioxide formation, and ammonia decomposition, respectively are kept at a minimum. In the example given, approximately 10% decomposition takes place and about 19% of the ammonia passes through unreacted. The ammonia can be handled either by reaction with sulfuric acid for by-product ammonium sulfate, or by ammonia recycle. In one operation, mono-ammonium phosphate solution is used to sorb ammonia, and the resulting diammonium phosphate is partially decomposed to recover ammonia for recycle.

The ammonia absorber overhead is sent to a hydrogen cyanide absorber and the aqueous hydrogen cyanide solution therefrom is sent to a stripper and fractionator for recovery of the hydrogen cyanide. In most cases, relatively little product is maintained in storage, and the hydrogen cyanide is taken directly to integrated process equipment for conversion to the ultimate commerical product.

III. Plant Emissions

A. Continuous Air Emissions

1. Process Off-Gas (Air Preheater Fuel)

A substantial quantity of hydrogen-rich hydrogen cyanide stripper off-gas from respondent 16-1 is delivered to the boiler house for use as fuel in process air preheaters. Hydrogen cyanide content of the off-gas runs 100 to 1000 PPM, though additional fuel (natural gas) is mixed with the relatively low heating value off-gas (74% inert), and complete combustion is presumed in the air heater burner. The only emissions under the stated conditions is a low level of nitrogen oxide (NO_x), calculated on the basis that 30% of the nitrogen in hydrogen cyanide can be expected to convert to NO_x. (See Table III with associated notes and summary Table VI.)

2. Process Sample Pot Vents

Streams from normal sample pot vents and other process equipment openings in respondent 16-1 plant are diluted with large quantities of air so that effluent stack concentrations average about 50 PPM (by vol) hydrogen cyanide. Variations from 25 to as high as 200 PPM can occur, at times, depending on leaking rupture discs or the like. Once-a-week sampling allows detection so that high levels do not persist. Dissipation from 120 to 150 foot stacks is designed to bring the concentration to safe levels. Sax (xiii) gives for hydrogen cyanide an ACGIH Threshold Limit Value (TLV) of 10 PPM in air. As an ordinary pollutant, the amount is small, but on TLV basis, one can calculate that sufficient HCN is emitted in one day to bring a 1000 cubic foot volume of air to the TLV level of 10 PPM (see Table III and associated notes, together with summary Table VI for details.)

3. Process Tank and Off-Gas Vents to Flares

These 16-1 plant streams are flared and include continuous small quantities (estimated 150 SCFM) of 0 up to 3% HCN by volume in nitrogen with concentration depending on tank fill timing, tank nitrogen purging, etc. Also included are continuous streams totalling 37,000 SCFM of the same composition, 100 to 1000 PPM hydrogen cyanide, as those in A-1 above. Flaring of these streams is assumed to effect complete combustion and on the assumption that 30% of hydrogen cyanide nitrogen converts to NO_x. NO_x after flaring is estimated to total 0.0016 tons per ton of hydrogen cyanide product. Table III and associated notes provide details.

B. Intermittent Air Emissions

Process Start-Up and Emergency Venting to Flares

Process start-up and emergency vents of feed gas and reactor effluent streams are sent to flares, normally for about 20 minutes at any one time and although several of these intermittent stream vents are tied into one flare stack in some cases, it is considered unlikely that more than one of these streams would "load up" a stack at any given time. Thus, combustion is assumed to be complete and the short term (~20 minutes at a time) emissions could raise a given stack NO_x content from the normal continuous levels below 0.0010 tons/ton hydrogen cyanide product to as high as 0.08 tons/ton when feed gas is being vented (assuming 60% of ammonia nitrogen converts to NO_x in a flare). When hydrogen cyanide, containing reactor effluent gas is being vented, the short term flare emissions can go to .026 tons of NO_x per ton of hydrogen cyanide product (assuming 30% of HCN nitrogen converts to NO_x in a flare). Since the intermittent start-up and emergency vent situations do not occur for long, calculations on an annual basis for all these intermittent streams together result in an estimate of a low overall flared stream total of 0.0016 tons of NO_x per ton of hydrogen cyanide product. (See summary Table VI and details in Table III with associated notes.)

C. Continuous Liquid Wastes

Liquid wastes are produced but the amount is unreported.

D. Solid Wastes

None reported.

E. Odors

Respondent 16-1, of course, is cognizant of the need to keep hydrogen cyanide emissions nil for safety of personnel and reports that odors from the plant are not a probelm.

E. Fugitive Emissions

None are reported. Only two small tanks are listed by respondent 16-1, and although they contain 5 - 10 wt. % hydrogen cyanide in water, they are maintained at 10° C, and back pressure controller vents connect to flares.

System leaks, if any, are such that they are "undetectable by material balances". Fugitive losses have never been determined, but due to hazard, any leaks discovered are quickly repaired.

IV. Emission Control

Combustion devices are the only type of emission control equipment reported by respondent 16-1 for the direct production of hydrogen cyanide from methane, ammonia and air. The details are to be found in Table IV, "Catalog of Emission Control Devices", with associated notes. In Table IV, all combustion devices are assigned two efficiency ratings:

(1) CCR - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ that react with pollutants to feed device}}{\text{lbs. of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

(2) SERR - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{\text{weighted pollutants in - weighted pollutants out}}{\text{weighted pollutants out}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Combustion Devices

Respondent 16-1 reports that 625 SCFM, a small proportion of the process off-gas from No. 1 train, is used as fuel for the HN-1 process air preheater. He indicates that a much larger flow, 16,000 SCFM, of No. 2 train process off-gas is similarly used, though no "device" information is provided for the latter. (All No. 3 train "off-gas" goes to HN-5 flare.)

Except for vents identified as sample pot vents, etc., which are simply diluted with large quantities of air (see previous Section III), the remaining vent streams are flared. In all cases, the "emission control" device, whether it be the gas-fired preheater HN-1 or the four indicated flares, is assumed to bring about complete combustion.

Where hydrogen cyanide is present, the level is low in the overall stream being subjected to combustion, and no odor problem has been noted. Thus, the only pollutant that may be of any significance is NO_x. There are conflicting statements in the literature concerning the extent to which chemically-bound nitrogen is converted to NO_x in combustion devices. In large scale commercial boilers, heaters and steam generation equipment, high temperatures and significant residence time situations result in appreciably nitrogen fixations from the air; the contribution made under such circumstances, by fuel nitrogen is "relatively inconsequential" according to Robert T. Walsh in Chapter 9 of the HEW "Air Pollution Manual", Public Health Service Publication 999-AP-40.

On the other hand, R. W. Rolke, et al, in "Afterburner Systems Study", EPA Publication S-14121, page 204, suggests that under the lower temperature conditions found in afterburner operations, very little NO_x is formed from nitrogen in the air and "most of the chemically-bound nitrogen in the waste can be expected to form NO_x along with that formed by nitrogen fixation in the burner flame".

Another conclusion may be reached by calculation based on S. Gordon and B. J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Composition, Rocket Performance, etc.", (NASA-SP-173). From this source, it may be calculated that at 2000° F, less than one percent of the ammonia and about zero percent of the hydrogen cyanide will convert to NO_x at equilibrium.

For the combustion of waste, as practiced in the present operation, no definitive data appear to be available. Industry sources have indicated that in an incinerator, from 60 to perhaps as high as 80 percent of the nitrogen in ammonia can convert to NO_x when burned, whereas the conversion is lower, on the order half as much for the nitrogen in hydrogen cyanide. Hence, for the fuel stream, 60 percent of the ammonia and 30 percent of the HCN are assumed to go to NO_x. From general knowledge of flare operation, one might expect effective temperatures around 2000° F. If residence time at 2000° F were appreciable, higher conversion to NO_x might be expected, but under the short duration flare conditions, an assumption has been made here that about 10 percent of the chemically bound nitrogen goes to NO_x. Details are to be found in Table IV.

V. Significance of Pollution

It is recommended that no in-depth study of this process be undertaken. No new direct (Andrussow) process capacity is anticipated. In fact, as discussed earlier in this report, direct process capacity likely will be phased out, and any new demand for hydrogen cyanide will be supplied from excess by-product capacity in conjunction with acrylonitrile plants now on stream or to be built.

Since no new capacity is anticipated, the Significant Emission Index* for the direct route hydrogen cyanide process is zero.

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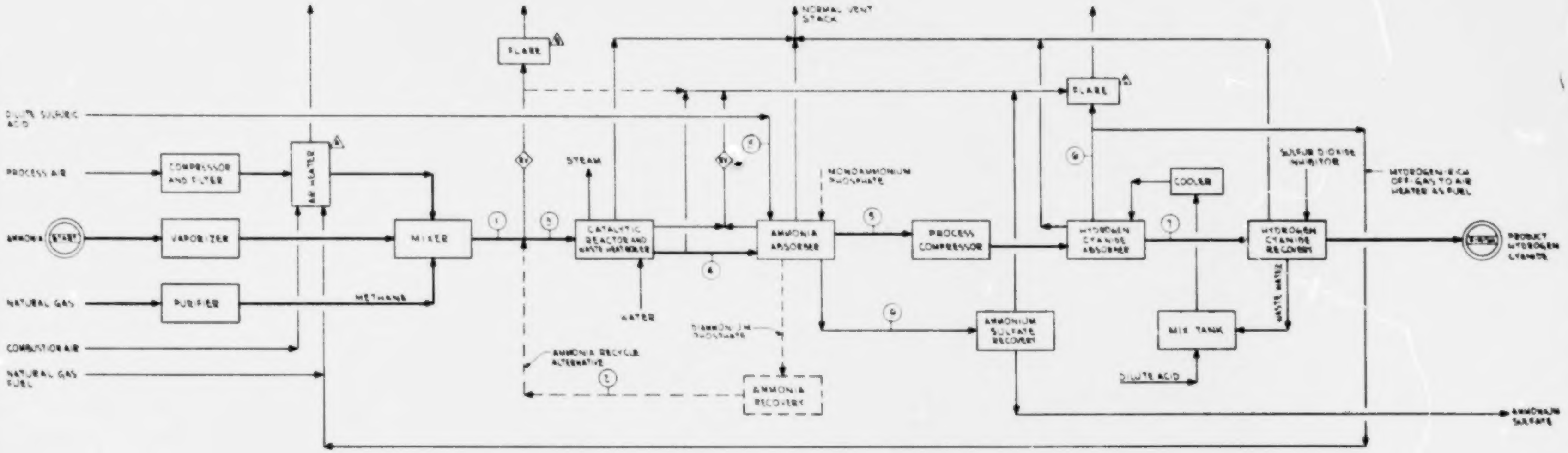
*For a discussion of Significant Emission Index concepts, see Appendix IV.

VI. Hydrogen Cyanide Producers

Since over 90% of the hydrogen cyanide produced in the United States today is destined for captive use, and often is immediately converted in integral production facilities, accurate tabulation of capacities and consumption figures is difficult. The relatively new propylene acrylonitrile production process which provides approximately 0.175 pounds of hydrogen cyanide by-product per pound of acrylonitrile (xiv), (instead of a requirement of over 0.5 pounds per pound for the old ethylene oxide or acetylene processes) has completely changed the picture for hydrogen cyanide. Following is a listing of direct and by-product hydrogen cyanide producers with plant locations and capacities: (x, xi, xii)

Company	Location	Annual Capacity 4/1/71 MM Lbs.	Process	Remarks
American Cyanamid Co.	Fortier, La.	27	By-product	Captive
Dow Chemical Co.	Freeport, Texas	5	Direct	Captive
E. I. duPont	Beaumont, Texas	30	By-product	Captive
" "	Memphis, Tenn.	115	Direct	Partly captive
" "	" "	27	By-product	Captive
" "	Victoria, Texas	(40)(1)	Direct	Captive
" "	La Place, La.	(20)(1)	Direct	Captive
B. F. Goodrich Co.	Calvert City, Ky.	7	By-product	Merchant
Hercules, Inc.	Glens Falls, N. Y	(2)(1)	Direct	Captive
Monsanto Co.	Alvin (Choc. Bayou), Tx.	56	By-product	Captive
" "	Texas City, Texas	75	Direct	Captive
Rohm & Haas Co.	Deer Park, Texas	155	Direct	Captive
Vistron (Std. Ohio)	Lima, Ohio	30	By-product	Merchant

(1) Based on January, 1971 CEH estimate including certain captive use approximations noted.


DILUTE SULFURIC ACID
PROCESS AIR
AMMONIA
START
NATURAL GAS
COMBUSTION AIR
NATURAL GAS FUEL
COMPRESSOR AND FILTER
VAPORIZER
PURIFIER
AIR HEATER
METHANE
MIXER
FLARE
STEAM
CATALYTIC REACTOR AND WASTE HEAT BOILER
WATER
AMMONIA RECYCLE ALTERNATIVE
AMMONIA RECOVERY
DIAMMONIUM PHOSPHATE
NORMAL VENT STACK
MONOAMMONIUM PHOSPHATE
AMMONIA ABSORBER
PROCESS COMPRESSOR
AMMONIUM SULFATE RECOVERY
HYDROGEN CYANIDE ABSORBER
COOLER
MIX TANK
DILUTE ACID
SULFUR DIOXIDE INHIBITOR
HYDROGEN CYANIDE RECOVERY
WASTE WATER
HYDROGEN-RICH OFF-GAS TO AIR HEATER AS FUEL
PRODUCT HYDROGEN CYANIDE
AMMONIUM SULFATE
1
2
3
4
5
6

NOTES

1. NUMBERED STREAMS - ① - IDENTIFY MATERIAL BALANCE ENTRIES (TABLE I)
2. LETTERED STREAMS - △ - IDENTIFY EMISSION CONTROL DEVICE (TABLE II)
3. INTERRUPTED STREAMS - ◇ - INDICATE INTERMITTENT FLOW STREAMS FOR START-UP AND EMERGENCY RELIEF VENTING.
4. THE CONFIGURATION SHOWS ALTERNATIVE AMMONIUM SULFATE BY-PRODUCT OR AMMONIA RECYCLE, AND DOES NOT REPRESENT A PARTICULAR PRODUCER'S FLOW DIAGRAM.

FOR
ENVIRONMENTAL PROTECTION AGENCY
CONTRACT NO. 68-02-0255

PREPARED BY
CATALYTIC, INC.
ENGINEERING DEPARTMENT PHILADELPHIA, PENNA.

FIGURE HN-1
SIMPLIFIED BLOCK FLOW DIAGRAM
HYDROGEN CYANIDE BY THE ANDRUSSOW PROCESS

SCALE	NONE	DATE
DRAWN BY	MMP	9-5-73
CHECKED BY	EBC	9-5-73
CATALYTIC APPROVAL		
CLIENT APPROVAL	DMP	9-4-73

CONTRACT NO. 42030
F.S. NO. 415
DWG. NO. R-220
REV. NO. A

TABLE HCN-I
BASIC CHEMISTRY
OF
ANDRUSSOW HYDROGEN CYANIDE PROCESS

MAIN REACTION

Reaction I. Controlled Catalytic Oxidation of Methane and Ammonia

$$2\ CH_4 + 3\ O_2 + 2\ NH_3 \xrightarrow[\text{Catalyst}]{} 2\ HCN + 6\ H_2O$$

Precious
Metal
Catalyst

SECONDARY REACTIONS

Reaction II. Partial Oxidation of Methane

$$CH_4 + O_2 \longrightarrow CO + H_2O + H_2$$

Reaction III. Complete Oxidation of Methane

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

Reaction IV. Dissociation of Ammonia

$$2\ NH_3 \longrightarrow N_2 + 3\ H_2$$

TABLE HCN-II
HYDROGEN CYANIDE BY THE ANDRUSSOW PROCESS
MATERIAL BALANCE
TONS/TON OF HYDROGEN CYANIDE PRODUCT

Stream No. (Fig. HN-1)	1	2	3	4	5	6	7	8	9
Stream Name	Fresh Feed	Recycle Ammonia (2)	Total Feed	Reactor Effluent	Ammonia Absorber Overhead	HCN Absorber Overhead (Vent)	HCN Absorber Bottoms to Fractionator	Acid Inlet	Ammonia Absorber Bottoms
Methane	.9626		.9626	.0085	.0085	.0085	0	0	0
Ammonia	.8679	.1991 (2)	1.0670	.1991	0	0	0	0	0
Oxygen	2.5553		2.5553	0	0	0	0	0	0
Nitrogen	8.0352		8.0352	8.2282	8.2282	8.2282	0	0	0
Hydrogen				.0829	.0829	.0829	0	0	0
Hydrogen Cyanide				1.0062	1.0062	.0062	1.0000	0	0
Carbon Dioxide				.0703	.0703	.0703	0	0	0
Carbon Monoxide				.5813	.5813	.5813	0	0	0
Water				2.4436			+ x (1)		
Sulfuric Acid	(.5739) (2)							.5739 (2)	
Ammonium Sulfate									.7730 (2)
Total	12.4210 (3)	.1991	12.6201	12.6201	9.9774	8.9774	1.0000 + x (1)	.5739	.7730

(1) Conversion and selectivity are based on information provided in Kirk-Othmer, 2nd Edition (1964), Vol. 6, pages 577-578: mol % methane conversion to HCN is 62%, ammonia conversion is taken at 59%, 19% of the ammonia passed thru unreacted, 10% decomposes and ultimate hydrogen cyanide yield is 73% on ammonia; polymer or carbon formation is assumed negligible and the ammonia absorber is assumed 100% efficient.

(2) Quantity of water in stream dependent on tower operating conditions.

(3) Total fresh feed figure excludes sulfuric acid, unreacted ammonia may be recycled or recovered as ammonium sulfate.

TABLE HCN-II-A
PRODUCTION OF HYDROGEN CYANIDE BY THE ANDRUSSOW PROCESS
GROSS HEAT BALANCE

Basis: Material Balance, Table II and reactions (vii, viii) shown in Table I, producing 1.0000 lb. hydrogen cyanide.

Catalytic Reactor Section, including waste heat boiler.

Heat Out

Heat exchange to cool products to 80° F	10,984	BTU/lb. hydrogen cyanide
Losses and heat required for steam generation in waste heat boiler	7,926	BTU/lb. hydrogen cyanide
Total	18,910	BTU/lb. hydrogen cyanide

Heat In

Reaction I - Exotherm producing	1.0000 lb.	HCN	-	7,570
Reaction II " "	0.5813 lb.	CO	-	2,481
Reaction III " "	0.070 lb.	CO_2	-	552
Reaction IV Endotherm "	.1930 lb.	N_2	-	(272)

Overall Exotherm ex Reaction I - IV	10,331	BTU/lb. hydrogen cyanide
Sensible heat of incoming charge	8,579	BTU/lb. hydrogen cyanide
Total	18,910	BTU/lb. hydrogen cyanide

TABLE HCN-III
NATIONAL EMISSIONS INVENTORY
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)

Page 1 of 4

Plant EPA Code No.	16-1
Capacity - Tons of HCN/Yr.	83,000
Average Production - Tons HCN/Yr.	
Quarterly Production Variation, % of Max.	0

Emissions to Atmosphere Stream	Product Recovery & Purification Section Off-Gas (Air Heater Fuel)	Start-Up and Emergency Feed Gas Venting	Start-Up & Emergency Reactor Effluent & Continuous Process Tank & Off-Gas Vents	Process Tank & Process Off-Gas Vents
Plant Train No.	1	1	1	1
Flow - Lb./Hr.	5,350	21,600	112,900	95,200
Flow Characteristics - Continuous or Intermittent	Continuous	Intermittent	Intermittent	Continuous
If Intermittent - Hrs./Yr. Flow		16	48	
Composition - Tons/Ton of Hydrogen Cyanide				
Methane				
Ammonia				
Nitrogen	1.408	.5396	(3)	3.2022
Oxygen				
Hydrogen				
Hydrogen Cyanide	.0015			
Carbon Dioxide		.1794		.4193
Carbon Monoxide	.0677			
Water		.2468		.6290
Sample Tap Location	None	None	None	None
Date or Frequency of Sampling	Never	Never	Never	Never
Type of Analysis	Calc'd	Calc'd	Calc'd	Calc'd
Odor Problem			Not Applicable	
Vent Stacks				
Flow - SCFM/Stack	1250 (1)	5250	27,400	22,550
Number	1	1	1	1
Height - Feet	85	76.5	76.5	76.5
Diameter - Inches	54	24	24	24
Exit Gas Temperature, °F	?	?	?	?
Emission Control Devices				
Type - Incinerator				
Flare		Yes	Yes	Yes
Scrubber				
Other	Air Heater			
Catalog I. D. Number	HN-1	HN-2	HN-3	HN-3
Total Hydrocarbon Emissions - Ton/Ton Hydrogen Cyanide	0	0	0	0
Total Particulates & Aerosol - Ton/Ton Hydrogen Cyanide	0	0	0	0
Total NO$_x$ (8) - Ton/Ton Hydrogen Cyanide	.00002 (8)	.009 (3) (8)	.006 (3) (8)	.0001 (8)
Total SO$_x$ - Ton/Ton Hydrogen Cyanide	0	0	0	0
Total CO Emissions Ton/Ton Hydrogen Cyanide	0	0	0	0

TABLE HCN-III
NATIONAL EMISSIONS INVENTORY
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)

Page 2 of 4

Plant EPA Code No.		16-1		
Capacity - Tons of HCN/Yr.		83,000		
Average Production - Tons HCN/Yr.				
Quarterly Production Variation, % of Max.		0		
Emissions to Atmosphere				
Stream	Process Sample Pot Vents	Product Recovery & Purification Section Off-Gas (Air Heater Fuel)	Process Off-Gas Vent	Process Tank & Process Off-Gas Vents
Plant Train No.	1	2	2	2 & 3
Flow - Lb./Hr.	296,000	137,000	17 800	48,700
Flow Characteristics - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow				
Composition - Tons/Ton of Hydrogen Cyanide				
Methane				
Ammonia				
Nitrogen	10.1493	3.6042	.5977	1.6367
Oxygen	3.0660			
Hydrogen				
Hydrogen Cyanide	.0006			
Carbon Dioxide		1.2927	.0783	.2143
Carbon Monoxide				
Water		1.2210	.1174	.3215
Sample Tap Location	Accessible	None	None	None
Date or Frequency of Sampling	Weekly	Never	Never	Never
Type of Analysis	GLC	Calc'd.	Calc'd.	Calc'd.
Odor Problem	No		Not Applicable	Not Applicable
Vent Stacks				
Flow - SCFM/Stack	65,000	16,000 (5)	4 200	11,500
Number	1	2	1	1
Height - Feet	150	?	24	110
Diameter - Inches	60	?	24	48
Exit Gas Temperature, °F	Ambient	?	?	?
Emission Control Devices	None			
Type - Incinerator				
Flare			Yes	Yes
Scrubber				
Other		Air Heater		
Catalog I. D. Number			HN-4	HN-5
Total Hydrocarbon Emissions - Ton/Ton Hydrogen Cyanide	.0006 (4)	0	0 (6)	0
Total Particulates & Aerosol - Ton/Ton Hydrogen Cyanide	0	0	0	0
Total NO_x (8) - Ton/Ton Hydrogen Cyanide	0	.0006	.00004	.00005
Total SO_x - Ton/Ton Hydrogen Cyanide	0	0	0	0
Total CO Emissions - Ton/Ton Hydrogen Cyanide	0	0	0	0

TABLE HCN-III
NATIONAL EMISSIONS INVENTORY
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)

Page 3 of 4

Plant EPA Code No.		16-1	
Capacity - Tons of HCN/Yr.		83 000	
Average Production - Tons HCN/Yr.			
Quarterly Production Variation, % of Max		0	
Emissions to Atmosphere			
Stream	Start-Up or Emergency Feed-Gas Relief & Continuous Process Tank & Process Off-Gas Vents	Start-Up or Emergency Feed Gas Relief & Continuous Process Tank & Process Off-Gas	Start-Up or Emergency Reactor Effluent Relief & Continuous Process Tank & Process Off-Gas Vents
Plant Train No.	2	3	2
Flow - Lb./Hr.	66,300	66,300	66,400
Flow Characteristics - Continuous or Intermittent	Intermittent	Intermittent	Intermittent
if Intermittent - Hrs./Yr. Flow	12	8	40
Composition - Tons/Ton of Hydrogen Cyanide			
Methane			
Ammonia			
Nitrogen	+	+	+
Oxygen			
Hydrogen			
Hydrogen Cyanide			
Carbon Dioxide	+	+	+
Carbon Monoxide			
Water	+	+	+
Sample Tap Location	None	None	None
Date or Frequency of Sampling	Never	Never	Never
Type of Analysis	Calc'd. (6)	Calc'd. (6)	Calc'd. ([illegible])
Odor Problem	Not Applicable	Not Applicable	Not Applicable
Vent Stacks			
Flow - SCFM/Stack	15,900	15,900	16,400
Number	1	1	1
Height - Feet	110	110	110
Diameter - Inches	48	48	48
Exit Gas Temperature - °F	?	?	?
Emission Control Devices			
Type - Incinerator			
Flare	Yes	Yes	Yes
Scrubber			
Other			
Catalog I. D. Number	HN-5	HN-5	HN-5
Total Hydrocarbon Emissions - Ton/Ton Hydrogen Cyanide	0 (6)	0 (6)	0
Total Particulates & Aerosol - Ton/Ton Hydrogen Cyanide	0	0	0
Total NO_x (8) - Ton/Ton Hydrogen Cyanide	.02 (3) (8)	.02 (3) (8)	.006 (3) (8)
Total SO_x - Ton/Ton Hydrogen Cyanide	0	0	0
Total CO Emissions - Ton/Ton Hydrogen Cyanide	0	0	0

TABLE HCN-III
NATIONAL EMISSIONS INVENTORY
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)

Plant EPA Code No.	16-1		
Capacity - Tons of HCN/Yr.	83,000		
Average Production - Tons HCN/Yr.			
Quarterly Production Variation, % of Max.	0		
Emissions to Atmosphere			
Stream	Start-Up or Emergency Reactor Effluent Relief & Continuous Process Tank & Process Off-Gas Vents	Process Sample Pot Vents	Process Sample Pot Vents
Plant Train No.	3	2	3
Flow - Lb./Hr.	66,400	296,000	18,200
Flow Characteristics - Continuous or Intermittent	Intermittent	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow	24		
Composition - Tons/Ton of Hydrogen Cyanide			
Methane			
Ammonia			
Nitrogen	+	10.1493	6246
Oxygen		3.0660	.1887
Hydrogen			
Hydrogen Cyanide		.0006	.00004
Carbon Dioxide	+		
Carbon Monoxide			
Water	+		
Sample Tap Location	None	Accessible	None
Date or Frequency of Sampling	Never	Weekly	Never
Type of Analysis	Calc'd. (6)	GLC	Calc'd
Odor Problem	Not Applicable	No	No
Vent Stacks			
Flow - SCFM/Stack	16,400	65,000	4,000
Number	1	1	2 (alternating)
Height - Feet	110	150	120
Diameter - Inches	48	60	16
Exit Gas Temperature - °F	?	Ambient	Ambient
Emission Control Devices		None	None
Type - Incinerator			
Flare	Yes		
Scrubber			
Other			
Catalog I. D. Number	HN-5		
Total Hydrocarbon Emissions - Ton/Ton Hydrogen Cyanide	0	0006 (4)	00004 (4)
Total Particulates & Aerosol - Ton/Ton Hydrogen Cyanide	0	0	0
Total NO_x (8) - Ton/Ton Hydrogen Cyanide	.006 (3) (8)	0	0
Total SO_x - Ton/Ton Hydrogen Cyanide	0	0	0
Total CO Emissions - Ton/Ton Hydrogen Cyanide	0	0	0

EXPLANATION OF NOTES
TABLE HCN-III
NATIONAL EMISSIONS INVENTORY
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)

(1) Only a small proportion of the hydrogen containing off-gas stream from No. 1 train is sent to the air heater, remainder is flared.

(2) Intermittent stream flow and instantaneous ton/ton concentrations indicated in this column apply only during the hours/year shown.

(3) Total vent flows when flaring start-up or emergency reactor effluent for perhaps a 20 minute period at any one time along with continuous vents indicated, total weight and volume flows as well as the instantaneous emission rate are shown for this relatively short time situation, though weights of individual gases are not indicated, since air input is assumed to remain unchanged. Complete combustion is assumed.*

(4) Pollutant in this stack effluent is solely the very toxic HCN, which, according to N. Irving Sax (xiii), has an American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 10 PPM or 11 milligrams per cubic meter of air. The air dilution in the stack brings the level to 50 PPM and safe dissipation is presumed, due to the 150 foot stack height.

(5) A large proportion of the hydrogen containing off-gas stream from No. 2 train is sent "to boilerhouse", therefore, not necessarily utilized in one particular heater, though two stacks for the process air heater were indicated. Complete combustion is assumed. All off-gas from No. 3 train is sent to flare.

(6) Complete combustion is assumed.

(7) Start-up and emergency relief streams are intermittent as indicated and for brief periods of perhaps 20 minutes in each instance, are combined with the continuous stream for flare (HN-5), the respondent reports that flow from more than one of these intermittent streams at one time is unlikely, hence, only one at a time is shown in combination in Table III.

(8) The questionnaire respondent 16-1, provided no information on NO_x. The figures given for NO_x in Table III (and the SERR figures in Table IV) are Houdry estimates based on the assumption that (a) NO_x conversion from ammonia is 60% of the stoichiometric amount, and (b) NO_x conversion from hydrogen cyanide is 30% of stoichiometric. Contribution to NO_x by fixation of nitrogen from the air is negligible (see Section VI discussion).

*Except for NOx procution, see Section VI discussion.

TABLE HCN-IV
CATALOG OF EMISSION CONTROL DEVICES
HYDROGEN CYANIDE BY THE ANDURSSOW PROCESS

Page 1 of 2

Plant Section (Process Train No.)	Process Air Heater (No. 1)	Feed Gas (No. 1)	Process Tanks & Process Off-Gas (No. 1)	Same & Reactor Effluent Start-Up & Emergency (No. 1)
INCINERATION DEVICES	Continuous	~16 hrs./yr.	Continuous	~48 hrs./yr.
EPA Code No. for plant using	16-1	16-1	16-1	16-1
Flow Diagram (Fig. 1) Stream I. D.	A	B	C	C
Device I. D. No.	HS-1	HS-2	HS-3	HS-3
Purpose - Control Emission of	Hydrogen Cyanide	Methane & Ammonia	Methane & Hydrogen Cyanide	Hydrogen Cyanide & Methane
Combustion Device - Flare		Yes	Yes	Yes
Incinerator				
Other	Air Heater			
Materials to Incinerator - SCFM (lb./hr.)	625	4440	22,550	27,400
Auxilliary Fuel Req'd. (Excl. Pilot)	For additional Heat	None	None	None
Type	Nat. Gas (1)			
Rate - BTU/hr.	6900			
Device or Stack Height - ft.	85	76.5	70.5	
Device or Stack Diameter - ft.	4.5	2	2	
Installed Cost - Mat'l. & Labor - $	165,000	47,100	41,750	
Installed Cost Based on "year" - dollars	1968	1968	1968	
Installed Cost - Mat'l. & Labor ¢/lb. Hydrogen Cyanide/Yr.	.0994	.0294	.0252	
Operating Cost - Annual - $ (1972)	500	1800	3300	
Operating Cost - ¢/lb. of Hydrogen Cyanide	.0003	.0011	.0020	
Efficiency - % - CCR	100 (1)	100 (2)	100 (2)	
Efficiency - % - SERR	84 (3) (6)	78 (3) (4)	95 (3) (4)	95 (3) (4)

TABLE HCN-IV
CATALOG OF EMISSION CONTROL DEVICES
HYDROGEN CYANIDE BY THE ANDRUSSOW PROCESS

Page 2 of 2

Plant Section (Process Train No.) INCINERATION DEVICES	Process Off-Gas (5) (No. 2) Continuous	Process Tanks & Process Off-Gas (No. 2 & 3) Continuous	Feed Gas Vent & HN-5 Continuous Vent (No. 2 & 3) 1 ~12 or 8 hrs./yr.	Reactor Effluent & HN-5 Continuous Vent (No. 2 & 3) ~40 or 24 hrs./yr.
EPA Code No. for plant using	16-1	16-1	16-1	16-1
Flow Diagram (Fig. 1) Stream I. D.	C	C	C	C
Device I. D. No.	HN-4	HN-5	HN-5	HN-5
Purpose - Control Emission of	Methane & Hydrogen Cyanide	Hydrogen Cyanide & Methane	Hydrogen Cyanide & Ammonia & Methane	Hydrogen Cyanide & Methane
Combustion Device - Flare	Yes	Yes	Yes	Yes
Incinerator				
Other				
Materials to Incinerator - SCFM (lb./hr.)	4,200	11,500	15,900	16,400
Auxilliary Fuel Req'd. (Excl. Pilot)	None	None	None	None
Type				
Rate - BTU/hr.				
Device or Stack Height - Ft.	74		110	
Device or Stack Diameter - Ft	2		4	
Installed Cost - Mat'l. & Labor - $	30,600		65,000	
Installed Cost Based on "year" - dollars	1958		1972	
Installed Cost - Mat'l. & Labor - ¢/lb. Hydrogen Cyanide/Yr.	.0184		.0392	
Operating Cost - Annual - $ (1972)	3100		3800	
Operating Cost - ¢/lb. of Hydrogen Cyanide	.0019		.0023	
Efficiency - % - CCR	100 (2)	100 (2)	100 (2)	100 (2)
Efficiency - % - SERV	95 (3) (4)	95 (3) (4)	79 (3) (4)	95 (3) (4)

EXPLANATION OF NOTES
TABLE HCN-IV
CATALOG OF EMISSION CONTROL DEVICES
HYDROGEN CYANIDE BY THE ANDURSSOW PROCESS

(1) Air heater HN-1 is not primarily a control device, it is fueled with 123 SCFM natural gas and, to recover heating value, 625 SCFM of waste process (nitrogen-diluted) off-gas containing hydrogen, carbon monoxide, a small amount of methane, and about 600 PPM hydrogen cyanide, all of which is presumed to undergo complete combustion.

(2) Complete hydrocarbon combustion is assumed.

(3) The % SERR shown here ignores the presence of methane.

(4) Calculations in this report are based on the assumption that flare temperature is 2000° F, and about 10 percent of the chemically bound nitrogen converts to NOx.

(5) Only one-fourth of the 16-1 plant off-gas from No. 2 train is flared, the remainder being sent to the boiler house, presumably to heat process air as was done in device HN-1 for No. 1 train.

(6) For this fuel stream, calculations are based on 60 percent of ammonia nitrogen and 30 percent of hydrogen cyanide nitrogen converting to NOx. (See Section IV.)

TABLE HCN-V
NUMBER OF NEW PLANTS BY 1980
MM LBS./YR.

	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be added by 1980	Economic Plant Size	Number of New Units
By-product Processes	177	37 (a)	140		510 (b)	360	(b)	(b)
Direct Process	412	210 (a)	202		202	0		0
Total	589	247	342	430	712	360		

(a) Arbitrary estimates with the assumption that roughly half the direct process producers will maintain operations for captive use.

(b) Acrylonitrile plant of economic 200 MM lb./year capacity has capability for ~35 MM lb./year of hydrogen cyanide by product (xiv). Not all acrylonitrile producers recover the hydrogen cyanide.

TABLE HCN-VI
EMISSION SOURCE SUMMARY
TON/TON OF HYDROGEN CYANIDE

Emission	Source				
	Process Off-Gas to Air Preheaters	Process Start-up and Emergency Reactor Effluent	Process Sample Pot Vents	Process Tank & Process Off-Gas Vents	Fugitive Emissions
Hydrocarbons	0	0	.0012 (c)	0	0
Particulates & Aerosol	0	0	0	0	0
NO_x	.0007 (a)	.0001 (b)	0	.0002 (d)	0
SO_x	0	0	0	0	0
CO	0	0	0	0	0

(a) NO_x estimate, deriving from burning of hydrogen cyanide in hydrogen-rich process off-gas used for air preheater fuel

(b) NO_x estimate from flaring of hydrogen cyanide and ammonia in streams and calculated on annual tonnage basis from instantaneous emission figures of Table III, according to hours per year there given.

(c) Actually hydrogen cyanide.

(d) NO_x estimate from flaring of hydrogencyanide content of streams.

TABLE HCN-VII
WEIGHTED EMISSION RATES

Chemical - Hydrogen Cyanide

Process - Direct (Andrussow) ex methane, ammonia and air.

Increased Capacity by 1980 - None using direct process. New and replacement capacity for hydrogen cyanide is expected to derive from new acrylonitrile plant installations.

Direct Process - Significant Emission Index = 0 MM lbs./year.

TABLE HCN-VIII - REFERENCES

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Isocyanates via Amine Phosgenation

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I. Introduction

This survey report covers the production of aromatic di-and poly-isocyanates. Although other isocyanates are commercially available (aliphatic, alicyclic di-& poly-isocyanates and mono-isocyanates) the aromatic based isocyanates account for almost the entire market. Of the aromatic isocyanates, three particular compounds comprise over 90% of the production. These are TDI (toluene diisocyanate 2,4 - and 2,6 - isomers), PMPPI (polymethylene polyphenylisocyanate) and MDI (4,4'-methylenediphenyl isocyanate). Manufacture of these three isocyanates is covered in this report.

Development by Farhenfabriken Bayer A. G. of a diisocyanate - polyester system lead to the production of a foam similar to rubber latex foam and lit the fire of true commercialization for both isocyanates and foams. Toluene diisocyanate (TDI) was used rather universally; diols and triols were used for flexible foams, the more highly functional polyols for rigid foams. Flexible polyurethane foams are made mostly from 80/20 TDI (80/20 = % of the 2,4 and 2,6 isomers respectively). PMPPI is used in semi-flexible foams as in automotive safety cushioning and in rigid foams. MDI and 80/20 TDI are the major isocyanates used in polyurethane surface coatings, elastomers, fibers and other applications. Di & polyisocyanates account for the bulk of isocyanates consumed. Mono isocyanates are used as chemical intermediates, mostly to produce pesticides.

Isocyanates are made almost exclusively by the phosgenation of amines dissolved in a (chlorinated) aromatic solvent. The main pollutants from this process are HCl (by-product of the phosgenation reaction), traces of phosgene, which hydrolizes to HCl in moist air, chlorinated hydrocarbons and CO from the phosgene generation step. Since phosgene and CO are both quite poisonous, it appears that care has been exercised in pollution control. Continuous emissions have been reported from these plants, but they are relatively minor air polluters, although characteristically the emissions are odorous.

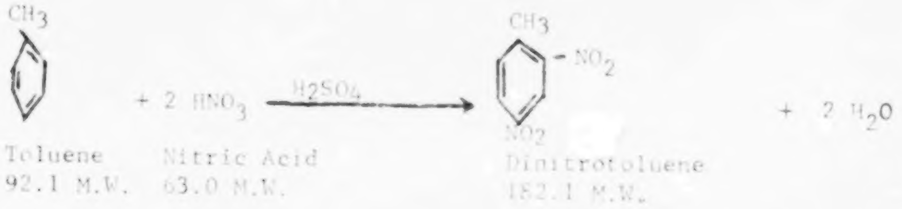
II. Process Description

Organic amines are reacted with phosgene in a suitable solvent to form the corresponding isocyanate and HCl as a by-product. Several side reactions and associated complications make this a far from simple reaction scheme. In the case of aromatic isocyanates, the subject of this survey report, all commercial manufacturing processes have the following approach:

1. Solution of the amine in an aromatic solvent such as xylene, monochlorobenzene or o-dichloro benzene.
2. This solution is mixed with a solution of phosgene ($COCl_2$) in the same solvent at a temperature below 140° F.
3. The resulting reaction mixture slurry is then digested in one to three stages for several hours at progressively increasing temperatures up to 390° F with the injection of additional phosgene.
4. The final solution of reaction products is fractionated to recover hydrogen chloride, unreacted phosgene and solvent for recycling, isocyanate product and distillation residue for incinerations.

The chemistry involved in the production of TDI, PMPPI and MDI is quite similar. TDI production from basic raw materials is shown for simplicity.

1. Di Nitration of Toluene

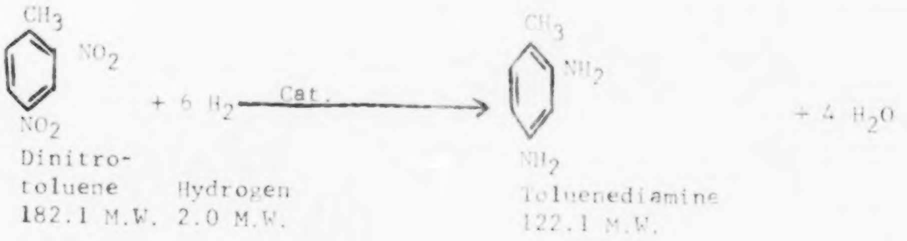


CH3
+ 2 HNO3
H2SO4
CH3
- NO2
NO2
+ 2 H2O
Toluene
92.1 M.W.
Nitric Acid
63.0 M.W.
Dinitrotoluene
182.1 M.W.

The nitration is done in two stages, mono-and di-. The product of the second nitration contains about 76% by weight of the 2,4 isomer (shown), 19% of the 2,6 isomer and the balance 2,3 and 3,4 isomers.

2. Reduction to an Amine

The mixture of dinitrotoluene isomers is fed to hydrogenators and reduced catalytically to toluene diamine (TDA), also a mixture of isomers.



CH3
NO2
NO2
+ 6 H2
Cat.
CH3
NH2
NH2
+ 4 H2O
Dinitro-
toluene
182.1 M.W.
Hydrogen
2.0 M.W.
Toluenediamine
122.1 M.W.

3. Phosgene Generation

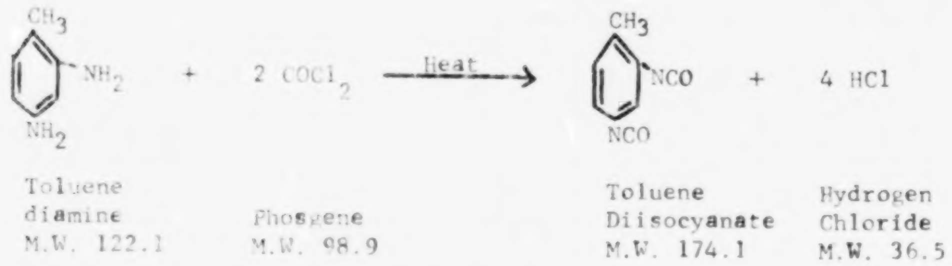
(a) $CH_4 + O_2 \longrightarrow CO + H_2$ (syn. gas)

Hydrocarbons other than methane may be used in this partial oxidation.

(b) $CO + Cl_2 \xrightarrow[\text{Cat.}]{\text{Carbon}} COCl_2$

Phosgene
M.W. 98.9

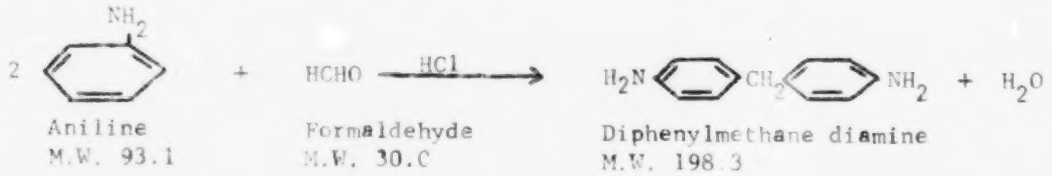
4. Phosgenation of the Amine


CH3
NH2
NH2
+
2 COCl2
Heat
CH3
NCO
NCO
+
4 HCl
Toluene diamine M.W. 122.1
Phosgene M.W. 98.9
Toluene Diisocyanate M.W. 174.1
Hydrogen Chloride M.W. 36.5

The TDI product contains about 80% 2,4 isomer and 20% 2,6 isomer.

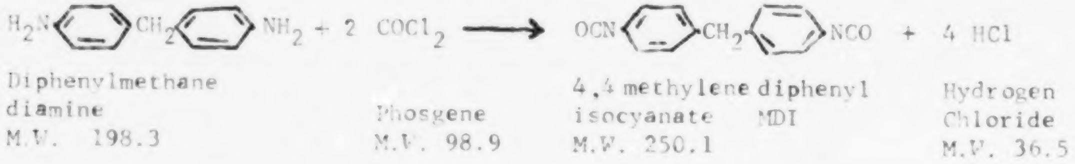
The manufacture of MDI and PMPPI begins with the acid condensation of aniline and formaldehyde to yield diphenyl methane amine (MDA).

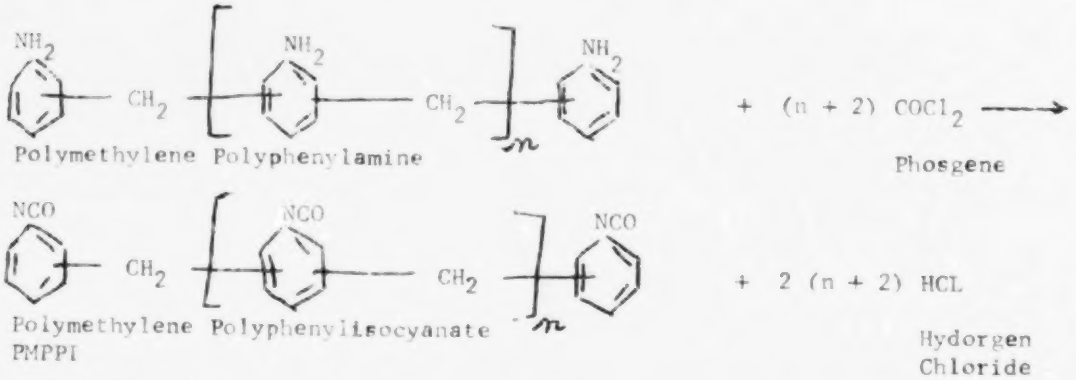
1. Acid Condensation


2
NH2
+
HCHO
HCl
H2N
CH2
NH2
+
H2O
Aniline M.W. 93.1
Formaldehyde M.W. 30.0
Diphenylmethane diamine M.W. 198.3

When PMPPI is the desired product, the amount of aniline and formaldehyde present and the reaction conditions are modified so that diphenyl methane diamine further condenses with aniline and formaldehyde to form tri-amine, tetramine and polyamines. This mixture is usually called polymethylene polyphenylamine.

2. Phosgenation of the Amines


H2N
CH2
NH2 + 2 COCl2
OCN
CH2
NCO
+
4 HCl
Diphenylmethane diamine M.W. 198.3
Phosgene M.W. 98.9
4,4 methylene diphenyl isocyanate MDI M.W. 250.1
Hydrogen Chloride M.W. 36.5


NH2
CH2
NH2
CH2
n
NH2
+ (n + 2) COCl2
Polymethylene Polyphenylamine
Phosgene
NCO
CH2
NCO
CH2
n
NCO
+ 2 (n + 2) HCL
Polymethylene Polyphenylisocyanate PMPPI
Hydorgen Chloride

MDI, like TDI, is purified by distillation. PMPPI need not be distilled.

III. Plant Emissions

A. Continuous Air Emissions

1. Phosgene Decomposer Vent

All plants have some sort of a phosgene decomposer. Usually, the HCL and $COCl_2$ go through a separator where the bulk of the phosgene is removed and recycled. In most cases, the next step is absorption of the HCl in water to give hydrochloric acid, which may either be sold or disposed of in some other manner. Residual quantities of phosgene and HCl go to a caustic scrubber where the HCl is absorbed as NaCl and the phosgene is decomposed to CO_2 and HCl and thence to NaCl and Na_2CO_3. Inert gases, CO (if present) and trace quantities of HCl and $COCl_2$ go to either a stack or an incinerator. In either case, a chloride aerosol emission is the end result. In plants which do not flare this stream, there is an emergency NH_3 stream which is injected into the stack if the $COCl_2$ content exceeds approximately 100 PPM. In this case, the phosgene is converted to ammonium chloride which is emitted as a particulate, albeit a non toxic particulate. None of the plants which had this emergency protection stated as to how often, if ever, it had been used.

The phosgene decomposers work very well and their efficiency is normally 99.9+%. However, in one case, respondent 17-10 reported an off-gas from the decomposer which contained two percent HCl and $COCl_2$. This is directed to the plant flare along with streams from other processes. HCl passes thru a flare unchanged and phosgene is probably decomposed to CO_2 and Cl_2. While the CCR* rating is nearly 100 percent for this stream, the Specific Emission Reduction Rating (SERR*) is nine percent reflecting only the change $COCl_2 \longrightarrow CO_2$ and Cl_2. Both $COCl_2$ and Cl_2 are counted as aerosols and the flare does practically nothing to this stream. Respondent 17-7 takes gas from his decomposers containing traces of CO and $COCl_2$ and runs it up a stack with 5000 CFM dilution air. This stack is also a fugitive emission collector and the purpose of the air dilution is personnel protection in the event of equipment failure or up-set.

Off-gas from most of these scrubbers (decomposers) is an occasional in-plant odor problem. In general, it can be concluded that emissions from phosgene decomposers are low, but pollution and hazard resulting from their malfunction is potentially significant.

2. Isocyanate Scrubber Vent

This vent is shown as coming from the TDI purification column overhead drum. This may or may not be true for each plant but it represents the general scheme for the process. This vent stream is mainly nitrogen (air) with small quantities of isocyanates and chlorinated hydrocarbons. A caustic scrubber is normally used to control pollution and both SE* and SERR are over 99.9 percent for these scrubbers. This stream contributes only a minor amount of pollution to the overall plant output, but does contribute to in-plant and out-of-plant odors.

*See page TDI-7 for definitions.

3. Residual Material Gas Scrubber

Scrubbed gas from this source contributes only trace quantities of pollutants and occasional in-plant odors. For those respondents who incinerate this residual stream, the incinerator off-gas contributes CO and hydrocarbon pollutants to the air and an occasional in-plant odor problem.

4. Miscellaneous Vents

These have been noted but contribute only trace quantities of pollutants. No numbers were available other than trace.

5. HCl Absorbers

Where the HCl is to be sold, it is absorbed in a chloride resistant packed column using water as the absorbing medium. A 35% acid can be recovered. Normally this scrubber would be followed by a caustic scrubber which would neutralize any HCl left in the gas plus decompose any phosgene in the stream.

If the HCl is not to be recovered, it may still be absorbed in water in a packed column but weak caustic is generally used. One respondent reports a novel scheme. In this case the HCl is not to be recovered but is fed into a large pit containing ground limestone and water. The HCl is converted to $CaCl_2$ and CO_2 is given off. The vent gas from this operation is reported as almost 100% air and CO_2 with trace quantities of HCl and H_2S from sulfur in the limestone. The H_2S traces cause an in-plant odor problem. One might suspect some HCl in the area since these are open pits but none was reported.

6. Plant Flares

Only two respondents reported venting streams to a flare. One stream is an off-gas from the TDA reactors which feed H_2 and dinitrotoluene. The gas consists mainly of ethanol, H_2, nitrogen and ammonia. Flared gas is reported as 100% CO_2, H_2O and N_2 so any efficiency rating of this unit is 100%. One would suspect some NO_x formed during the flaring.

The other respondent feeds a stream of inerts and HCl and $COCl_2$ to his plant flare. This was covered in Section III-1, Phosgene Decomposer Vent. It makes little sense to flare HCl and $COCl_2$ other than the dilution provided by other streams and the coversion of toxic $COCl_2$ to somewhat less toxic Cl_2. CCR on the flare is 100% but the SERR is a lowly nine percent. A stopgap operation. A better method should be used.

B. Intermittent Emissions

None reported.

C. Continuous Liquid Wastes

The amount of waste water varies considerably from plant to plant. All plants treat this waste water although the treatment may be described as minimal in two cases. Waste water runs between 0.5

and 50 gal./lb. TDI, the bulk being 0.5 to 5.0 gal./lb. In the MDI/PMPPI plants, the figure is much lower at 0.05 to 0.4 gals./lb.

D. Solid Wastes

Most TDI plants report a solid waste varying from 0.05 to 0.14 lbs./lb. TDI which is hauled away for landfill. Two respondents report no solid waste. For MDI, PMPPI a figure of 0 to 0.01 lbs./lb. applies. One respondent (TDIplant) occasionally burns this residue in the plant furnaces but no data were given on combustion efficiency or pollutants.

E. Odors

Most plants have an in-plant odor problem. Phosgene emissions are minimal, less than 100 PPM in the stack gas and many stacks are monitored to inject NH_3 into the vent stream if this figure is reached due to an upset. However, trace quantities of isocyanates are emitted and these compounds have rather strong and characteristic odors. Phenyl isocyanate has best been described as an offensive lachrymatory liquid, for example.

F. Fugitive Emissions

No respondent offered any estimate of fugitive emissions although several agreed that there were minor emissions at valves, joints and pump seals. One respondent keeps a vacuum system operable which is used to control emissions by sucking them up as they occur until the leak can be repaired. Many of the isocyanate storage tanks are nitrogen blanketed, venting to the air. All HCl storage tnaks vent thru a water scrubber. On the negative side, a minor number of isocyanate storage tanks have no vapor barrier and vent directly to the air. This could well be a source of odor.

G. Other Emissions

Only insignificant quantities of sulfur in the natural gas fuels used.

IV. Emission Control

The emission control devices that have been reported as being employed by the operators of the isocyanates by phosgenation plants are described in Table IV of this report. An efficiency has been assigned each device whenever data sufficient to calculate it have been available. Three types of efficiencies have been calculated.

(1) "CCR" - Completeness of Combustion Rating

$$\text{CCR} = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutants in device feed)}}{\text{lbs. of } O_2 \text{ theoretically capable of reacting}} \times 100$$

(2) "SE" - Specific Efficiency

$$\text{SE} = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$\text{SERR} = \frac{(\text{pollutant} \times \text{weighting factor*})\text{in} - (\text{pollutant} \times \text{weighting factor*})\text{out}}{(\text{pollutant} \times \text{weighting factor*})\text{in}} \times 100$$

*Weighting factor same as Table VII weighting factor.

Normally a combustion type control device (i.e., incinerator, flare, etc.) will be assigned both a "CCR" and an "SERR" rating, whereas a non-combustion type device will be assigned an "SE" and/or an "SERR" rating. A more complete description of this rating method may be found in Appendix V of this report.

A. Phosgene Decomposers

These units consist of one or two chloride resistant packed columns scrubbed with a nominal 10 percent caustic solution or recycle. In some cases water is the absorbing/decomposing medium. Efficiencies are usually 99+%. One respondent dilutes the off-gas because it is combined with the effluent from a fugitive "sniff" system. This keeps the total stream well under 100 PPM $COCl_2$. Another respondent's data indicate a 75 percent efficiency but the off-gas from this unit is sent to a flare where it is diluted with material from other sources. A more efficient decomposing system would seem to be in order.

Almost every respondent has made provision to kill any phosgene break thru because of a decomposer malfunction by injecting ammonia in the stack to form NH_4Cl. Assuming the use of some excess ammonia to completely neutralize the toxic $COCl_2$, this system would lay down a blanket of NH_4Cl particulate and also introduce ammonia vapor into the atmosphere. No one indicated how often this emergency system was used. Indications were that it was infrequent.

B. Isocyanate Fume Scrubbers

Without exception, all of these units are packed bed weak caustic (recycle) scrubbers and efficiencies are 99.9+%. However, there is usually a persistent in-plant odor problem associated with this source despite the high efficiency.

C. Residual Vent Scrubbers

These scrubbers are spray towers using water. Apparently the odor problem here is negligible. Some respondents incinerate the residual stream. See D.

D. Residual Incinerator

Two types of incinerators were described. The first appears to be a conventional fire-box combustion chamber and stack. The respondent gave no indication of any odor associated with the off-gas. The other respondent used what was referred to as a "pit" incinerator with excess combustion air. Although the data supplied gave an efficiency of 100 percent, an odor problem was reported as being associated with this incinerator. One can only conjecture that this problem could be solved if an incinerator with a fire-box and adequate combustion chamber were used instead of a "pit". Neither reported any NOx formation.

E. Flares

Two plants used flares. One plant flaring H_2 and ethanol vapors from manufacture of dinitrotoluene reported an efficiency of 100 percent, although this unit is strictly outside the scope of this report. The only potential unreported emission from this flare is NOx from either the combustion air or small quantities of NH_3 in the gas stream.

The other respondents flare was discussed in this section under A, since it received the phosgene decomposer off-gas. As stated, a flare is not an appropriate way to dispose of chlorides.

F. Miscellaneous

The unit under plant 17-7, Incineration and Dispersion Device, Table IV is a dilution stack and was mentioned in Section A. It does not decompose any HCl or $COCl_2$ which enters. It dilutes them and as such should be considered a personnel protection device rather than a pollution control device.

V. Significance of Pollution

On a weighted emission basis, a Significance Emission Index of 225 has been calculated for this process. This is on the lower end of the spectrum and as a result, no in-depth study of the process is recommended.

Methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from the new plants forecast up to 1980. The work is summarized in Tables V, VI and VII.

Isocyanates have had a tremendous growth throughout the 1960's. TDI, MDI and PMPPI account for over 90% of the total U. S. isocyanate production and polyurethane foams are the largest market for these materials. Isocyanates have grown is sales volume by 15-20% per year from 1965 to 1970. The projected growth rate for the period 1970 - 1975 is 8-12% per year.

Installed capacities of isocyanate plants seems to be generally overstated and, on the average, sales run about 85% of the published capacity. At the end of 1973, published capacity (Table VI) was 1088 million lbs./year or about 924 million lbs. production at 85%. If a 10%/year growth is assumed until 1980, installed capacity will then be 2120 million lbs., a production rate of about 1800 million lbs. (demand). This will require about 10 new plants of 100 million lbs. capacity each.

These numbers were used to calculate the SEI of 225. The major pollutants from this process are HCl and organic chlorides as aerosols and CO. There are odors associated with the various isocyanates, a rather unpleasant smelling family of compounds.

It should be noted that the reported data include a wide range in emissions In fact, one plant (17-6) reports an emission rate for hydrocarbons that is 40 times that used in the SEI calculation. If the large rate had been used, the SEI value would be greater than 400.

VI. Producers of Cyclic Isocyanates

The capacities and plant locations listed below are based on information provided by the questionnaires and literature. All capacities are in million of pounds per year.

Company	Location	Capacity, 1973
Allied Chemical	Moundsville, W. Va.	65
BASF	Geismar, La.	40
Du Pont	Deepwater, N. J.	105
Jefferson Chemical	Port Neches, Texas	50*
Kaiser	Gramercy, La.	20*
Mobay	New Martinsville, W. Va.	100
		100*
	Cedar Bayou, Texas	150
Olin	Ashtabula, Ohio	40
	Lake Charles, La.	90
Rubicon	Geismar, La.	31
		67*
Union Carbide	South Charleston, W. Va.	60
Upjohn	La Porte, Texas	170*

Total = 1,088

TDI = 681

PMPPI/MDI = 407*

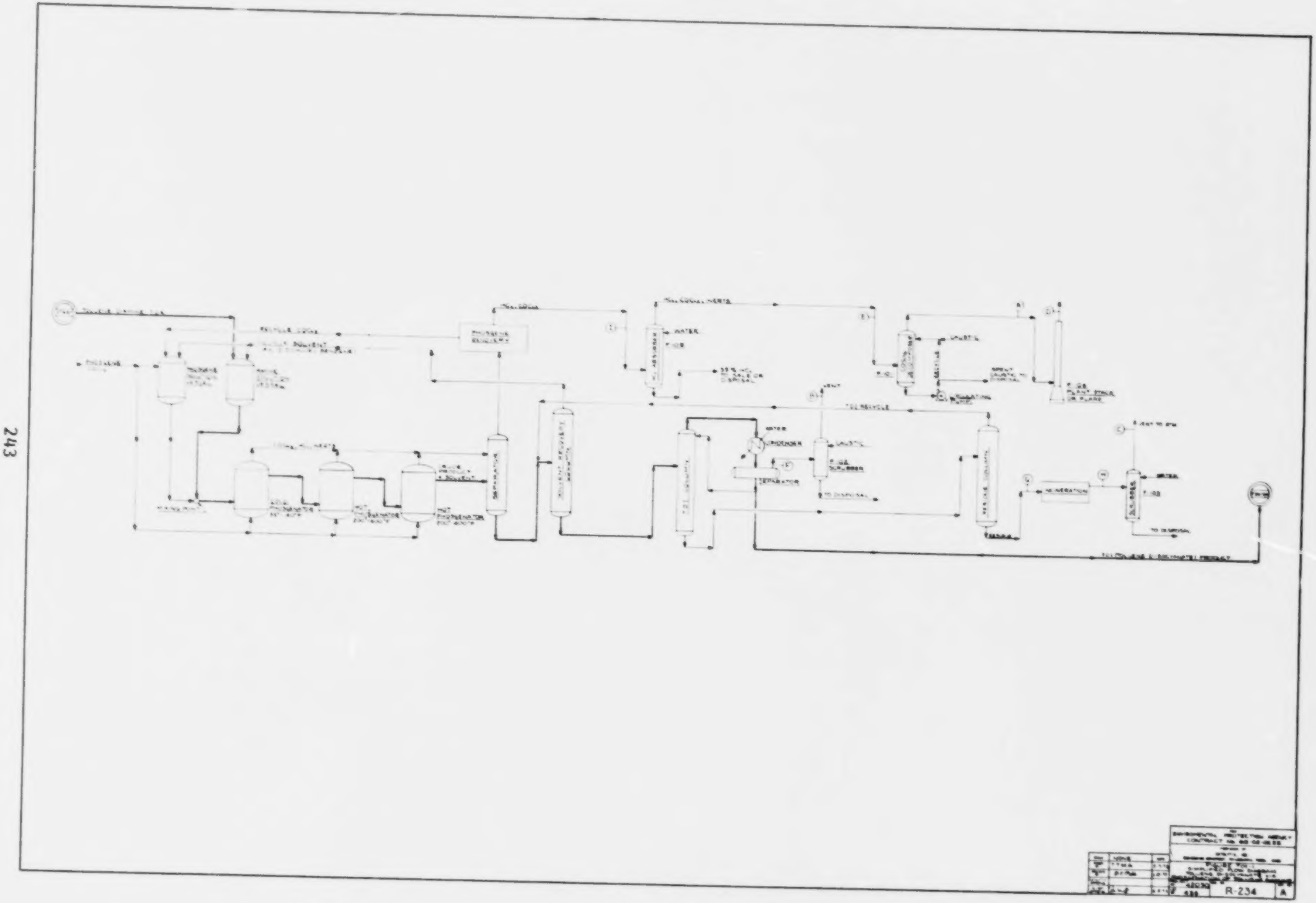

WATER
CAUSTIC
SPENT CAUSTIC TO DISPOSAL
PLANT STACK OR FLARE
TOL RECYCLE
VENT
CONDENSER
SEPARATOR
SCRUBBER
CAUSTIC
TO DISPOSAL
INCINERATION
WATER
TO DISPOSAL
R-234
A

TABLE TDI-1
ISOCYANATES

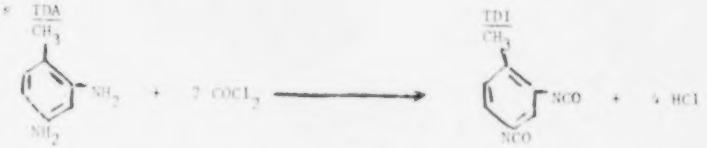
MATERIAL BALANCE - T/T ISOCYANATE

1. TDI production from TDA. Average of data from four respondents.

IN	Actual	Theo.+
Lb. TDA	0.884	0.702
Lb. $COCl_2$	1.448	1.136
Lb. Inserts	0.084	0.0
	2.416	1.838

OUT	Actual	Theo +
Lb. TDI	1.000	1.000
Lb. HCl (100%)	1.011	0.838
Lb. Residuals	0.067	0.0
Lb. Gas. Inert	0.020	0.0
Lb. Unaccounted for	0.318	0.0
	2.416	1.838

+Basis

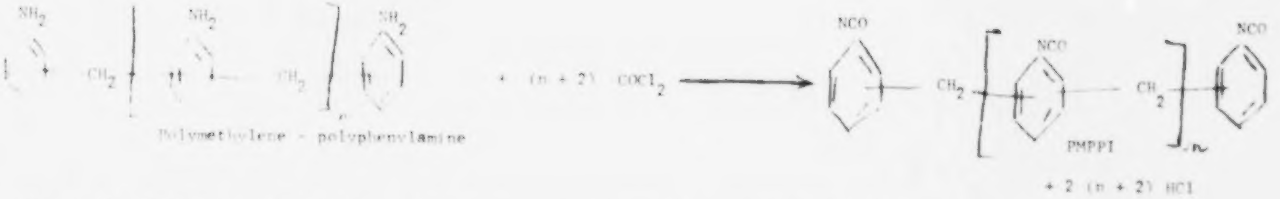

TDA
CH3
NH2
NH2
+ 2 COCl2
TDI
CH3
NCO
NCO
+ 4 HCl

2. MDI and PMPPI - production from MDA. Average of data from three respondents

IN	Actual	Theo.*
Lb. MDA	0.831	0.800
Lb. $COCl_2$	0.855	0.770
	1.686	1.570

Out	Actual	Theo.*
Lb. PMPPI (MDI)	1.000	1.000
Lb. HCl (100%)	0.597	0.570
Lb. Residuals	0.001	0.00
Lb. Unaccounted for	0.088	0.00
	1.686	1.570

*Basis


NH2
CH2
NH2
CH2
NH2
n
Polymethylene - polyphenylamine
+ (n + 2) COCl2
NCO
CH2
NCO
CH2
NCO
PMPPI
n
+ 2 (n + 2) HCl

if n=0, then diphenyl methane diamine (MDA) ⟶ 4,4 methylene diphenyl isocyanate (MDI)

TABLE TDI-II
ISOCYANATES

GROSS REACTOR HEAT BALANCE

There were no published data readily available to allow any kind of a heat balance to be calculated for this process.

TABLE TDI-III
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

Page 1 of 5

Plant EPA Code No.	17-1	
Capacity Tons Isocyanates/Yr.	100,000	
Range of Production - % of Max.	0	
Emissions to Atmosphere		
Stream	Phosgene Decomposer Vent Gas	Residue Gas Scrubber Vent
Flow - lb./Hr. (SCFM)	(9000)	
Flow Characteristic - Continuous or Intermittent	Continuous	
if Intermittent - Hrs./Yr.		
Composition - Ton/Ton Iso		
Hydrocarbons		
Nitrogen (Air)		
CO	0.016212	
CO_2	0.005628	No Data
Steam	0.008800	
$COCl_2$-Phosgene		
Chlorinated Hydrocarbons	0.000296	
HCl	0.002431	
Aniline		
Isocyanates		
H_2S, SO_x		
Particulates		
Vent Stacks		
Number	1	1
Height - Ft.	725	700
Diameter - Inches	12	6
Exit Gas Temperature - °F	212	70
SCFM/Stack	1000	?
Emission Control Devices	Scrubber	Scrubber
Analysis		
Date or Frequency of Sampling	Once per year	
Tap Location	In Stack	
Type of Analysis	GC, IR	
Odor Problem	N. C.	
Summary of Air Pollutants		
Hydrocarbons - Ton/Ton Iso.		N. C.
Aerosols - Ton/Ton Iso.		0.002431
NO_x - Ton/Ton Iso.		0.000296
SO_x - Ton/Ton Iso.		
CO - Ton/Ton Iso.		0.005628

TABLE TDI-III
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

Page 2 of 5

Plant EPA Code No.			17-2			
Capacity Tons Isocyanates/Yr.			20,000			
Range of Production - % of Max.			±8			
Emissions to Atmosphere						
Stream	Phosgene Decomposer Vent Gas	HCl Absorber	TDI Scrubber Vent	Residue Gas Scrubber Vent	CO Furnace Purge Vent	CO_2 Removal Regenerator Vent
Flow - Lb./Hr. (SCFM)	(8)	(27)	(28)	(870)	(180)	(414)
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Intermittent	Continuous
if Intermittent - Hrs./Yr.					?	
Composition - Ton/Ton Iso.						
Hydrocarbons						
Nitrogen (Air)	0.000200	0.006400	0.024234	0.843343		
CO					TR	
CO_2	0.011560	0.029800			0.266760	
Steam						0.236571
$COCl_2$ - Phosgene						
Chlorinated Hydrocarbons						
HCl						
Aniline						
Isocyanates						
H_2S, SO_x					TR	TR
Particulates						
Vent Stacks						
Number	1	1	1	1	1	1
Height - Ft.	45	50	70	17	98	66
Diameter - Inches	3	4	6	8	8	4
Exit Gas Temperature - °F	125	100	100	80	7	250
SCFM/Stack	8	27	28	870	0	309
Emission Control Devices	Scrubber	Absorber	Scrubber	Scrubber	None	None
Analysis						
Date or Frequency of Sampling	Occasional	Never	Occasional	Never	Never	Occasional
Tap Location	In Stack		in Stack			
Type of Analysis	GC		GC	Est	Est	Wet
Odor Problem	No	No	No	No	No	No
Summary of Air Pollutants						
Hydrocarbons - Ton/Ton Iso.						
Aerosols - Ton/Ton Iso.						
NO_x - Ton/Ton Iso.						
SO_x - Ton/Ton Iso.						TR
CO - Ton/Ton Iso.						TR

TABLE TDI-III
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

Page 3 of 5

Plant EPA Code No		17-3			17-8	
Capacity Tons Isocyanates/Yr		33,500			15,500	
Range of Production - % of Max		0			0	
Emissions to Atmosphere						
Stream	Phosgene Decomposer Vent Gas	MDI Fume Scrubber Vent	Distillation Scrubber Vent	Phosgene Decomposer Vent Gas	TDI Scrubber Vent	Residue Incinerator Vent
Flow - Lb./Hr. (SCFM)	1151	2080	223	(22)	242	(8300)
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous		
if Intermittent - Hrs./Yr						
Composition - Ton/Ton Iso						
Hydrocarbons						
Nitrogen (Air)	0.003548	1.02088	0.011657		0.058650	8.28672
CO	0.011759			0.021292		0.695137
CO_2						
Steam	0.101168		0.010846			0.338495
$COCl_2$ - Phosgene	TR	TR		TR		
Chlorinated Hydrocarbons				0.006654		
HCl						TR
Aniline			0.000023			
Isocyanates						
H_2S, SO_x						
Particulates						
Vent Stacks						
Number	No Data	No Data	No Data	1	1	No Data
Height - Ft	" "	" "	" "	55	76	" "
Diameter - Inches	" "	" "	" "	6	4	" "
Exit Gas Temperature - °F	" "	" "	" "	150	125	" "
SCFM/Stack	" "	" "	" "	7	1	" "
Emission Control Devices	Scrubber	Scrubber	Scrubber	Scrubber	Scrubber	Incinerator
Analysis						
Date or Frequency of Sampling						
Tap Location						
Type of Analysis						
Odor Problem	No	No	No	No	No	No
Summary of Air Pollutants						
Hydrocarbons - Ton/Ton Iso			0.000023			0.006654
Aerosols - Ton/Ton Iso			TR			
NO_x - Ton/Ton Iso						
SO_x - Ton/Ton Iso						
CO - Ton/Ton Iso			0.011759			0.716429

TABLE 101-111
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

Page 4 of 5

Plant EPA Code No.	17-4	17-9		17-6			
Capacity Tons Isocyanates/Yr.	13,000	85,000		20,000			
Range of Production - % of Max.	0	0		+ 8, - 16			
Emissions to Atmosphere							
Stream	MDI Recovery Unit Vent	Reactor Vent	Amine Scrubber Vent	Reactor Vent	Reactor Cond Vent	Phosgene Destruction Unit Off-Gas	Incinerator Stack Gas
Flow - Lb./Hr. (SCFM)	(50)	100	1200	(375)	(39.5)	(1833)	(9000)
Flow Characteristic - Continuous or Intermittent	Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous	Intermittent
If Intermittent - Hrs./Yr.	675 est						?
Composition - Ton/Ton Iso							
Hydrocarbons					TR	0.041326	TR
Nitrogen (Air)	0.004875	0.003517	0.406780	0.021442	0.027875	1.614425	8.507602
CO							
CO_2		0.000085		0.049513			0.115010
Steam		0.000636	0.144068	0.185965	0.005263	0.062183	0.024951
$COCl_2$ - Phosgene							
Chlorinated Hydrocarbons	0.000141	TR					
HCl	0.000044						
Aniline			TR				
Isocyanates	0.000150						
H_2S, SO_x							
Particulates	TR						TR
Vent Stacks							
Number	1	1	1	1	1	1	
Height - Ft.	50	Ground	50	175	Ground	130	Ground
Diameter - Inches	2	10	6	18	3' x 5'	12"	8' x 8'
Exit Gas Temperature - F°	Ambient	110°	110°	2000°	130°	102°	?
SCFM/Stack	50						
Emission Control Devices	None	None	Scrubber	Flare	None	Scrubber	Pit Incinerator
Analysis							
Date or Frequency of Sampling	Never	Never	Never	Never	Never	Never	Never
Tap Location	None	None	None	None	In Line	None	None
Type of Analysis	Estimate	Estimate	Estimate	Calculated	Calculated	Calculated	Calculated
Odor Problem	Yes	Yes	Yes	No	Yes	No	Yes
Summary of Air Pollutants							
Hydrocarbons - Ton/Ton Iso	0.000291		0.000291				0.041326
Aerosols - Ton/Ton Iso	0.000044		0.000044				
NO_x - Ton/Ton Iso							
SO_x - Ton/Ton Iso							
CO - Ton/Ton Iso							

TABLE TDI-III
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

Page 5 of 5

Plant EPA Code No.	17-7		17-10			
Capacity Tons Isocyanates/Yr	52,500		30,000			
Range of Production - % of Max	0		0			
Emissions to Atmosphere						
Stream	Plant Scrubber Stack	Residue Vent Gas	Plant Flare	TDI Reactor Emergency Vent	Residue Gas Vent	HCl Neut. Off-Gas
Flow - Lb./Hr. (SCFM)	(10,000)	(200)	1000	600	250	22,876
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent	Continuous	Continuous
if Intermittent - Hrs./Yr.				8		
Composition - Ton/Ton Iso.			(Calc'd.)			
Hydrocarbons				0.000002		
Nitrogen (Air)	4.103120	0.002419	0.126316	0.000070	0.006184	2.693947
CO	0.010429					
CO_2			0.003211		0.000499	0.258816
Steam		0.047555		0.000006	0.026316	0.060132
$COCl_2$ - Phosgene	0.000083		0.000921 (Cl_2)	0.000001	TR	
Chlorinated Hydrocarbons					TR	
HCl			0.001316		TR	0.001210
Aniline						
Isocyanates		0.000083		0.000001		
H_2S, SO_x						0.000092
Particulates	TR					
Vent Stacks						
Number	2	4	1	1	1	3
Height - Ft	160	60	110	60	80	20
Diameter - Inches	30"	4"	?	2"	2"	10"
Exit Gas Temperature - °F	Ambient	200°	1600°	212°	120°	100°
SCFM/Stack	5000	50				
Emission Control Devices	Scrubber	None	Scrubber & Incinerator	None	None	Limestone Neut.
Analysis						
Date or Frequency of Sampling	Continuous for $COCl_2$	Never	Never	Never	Never	Never
Tap Location	In Line	None	None	None	None	None
Type of Analysis	Calc'd	Est.	Calc'd.	Calc'd.	Calc'd	Calc'd.
Odor Problem	Yes	Yes	No	No	Yes	Yes
Summary of Air Pollutants						
Hydrocarbons - Ton/Ton Iso.						0.000002
Aerosols - Ton/Ton Iso.		0.000166				0.003448
NO_x - Ton/Ton Iso.						
SO_x - Ton/Ton Iso.						0.000092
CO - Ton/Ton Iso.		0.010429				

EXPLANATION OF NOTES
TABLE TDI-III
NATIONAL EMISSIONS INVENTORY
ISOCYANATES

1. Phosgene has been counted as an aerosol because in moist air, $COCl_2 \longrightarrow 2\ HCl + CO_2$. HCl has been routinely reported as an aerosol in other reports.

2. Chlorinated hydrocarbons, aniline and isocyanates have been counted as hydrocarbons.

3. Under "Type of Analysis", GC means gas chromatograph and IR means infra red analysis.

TABLE TDI-III
CATALOG OF EMISSION CONTROL DEVICES
ISOCYANATES

ABSORBER/SCRUBBERS					
EPA Code No. for plant using	17-1	17-1	17-2	17-2	17-2
Flow Diagram (Fig. TDI-1) Stream I, N	F	F	F	I	E
Device I. D. No.	F-101	F-102	F-101	F-105	F-102
Control Emission of	Phosgene	TDI Residue Gas	Phosgene	HCl	TDI Off-Gas
Scrubbing/Absorbing Liquid	Water	Water	Water	Water	10% NaOH
Type - Spray					
Packed Column	X	X	X	X	X
Tray Column					
Scrubbing/Absorbing Liquid Rate - GPM	120 - 150	15 - 20	80	19	?
Design Temperature (Operating Temperature) - F°	Ambient	Ambient	Ambient	<50° F	100
Gas Rate - SCFM (Lb./Hr.)	400 - 700	?	25 - 50	(4600)	28
T-T Height, Ft.	30	15	25	11	35
Diameter - Ft.	4 towers - 6 ft. each	1	3	1, 3	5 and 8 (1)
Washed Gases to Stack	Yes	Yes	Yes	Yes	Yes
Stack Height - Ft.	125'	200	45	50	70
Stack Diameter - In.	12	6	3	4	6
Installed Cost Mat'l. & Labor - $	250,000	10,500	7,500	199,000	293,000
Installed Cost based on "year" - $	1971	1971	1970	1968	1964
Installed Cost - $/lb. Isocyanate	0.375	0.0053	0.019	0.498	0.733
Operating Cost - Annual - $ (1972)	80,000	4,000	1,400	10,600	229,250
Value of Recovered Product - $/Yr.				400,000	
Net Operating Cost - $/lb.	0.040	0.002	0.0035	(0.97)*	0.573
Efficiency - % - SF	Insufficient Data	No Data	100	100	100
Efficiency - % - SFRK	Insufficient Data	No Data	100	100	100

ABSORBER/SCRUBBERS					
EPA Code No. for plant using	17-2	17-2	17-8	17-8	17-3
Flow Diagram (Fig. TDI-1) Stream I, N	F	E	F	E	F
Device I. D. No.	F-102	F-101	F-102	F-101	F-102
Control Emission of	TDI Residue Gas	Phosgene	Reactor Fumes	Phosgene	Reactor Fumes
Scrubbing/Absorbing Liquid	Water	10% Caustic	8% Caustic	8% Caustic	10% Caustic
Type - Spray	X				
Packed Column		X	X	X	X
Tray Column					
Scrubbing/Absorbing Liquid Rate - GPM	?	?	100	190	190
Design Temp. (Operating Temperature) - F°	80	70	150	125	125
Gas Rate - SCFM (Lb./Hr.)	870	5	200	2000	2000
T-T Height, Ft.	10	46	55 (ea)	76	81
Diameter - Ft.	2	2½	2 in series, 6'	4	4
Washed Gases to Stack	Yes	Yes	Yes	Yes	Yes
Stack Height - Ft.	12	66	55	76	81
Stack Diameter - In.	6	4	72	48	48
Installed Cost Mat'l. & Labor - $	16,000	86,000	139,271	44,318	38,630
Installed Cost based on "year" - $	1972	1964 - 1972	1966 - 1972	1966 - 1972	1972
Installed Cost - $/lb. Isocyanate	0.06	0.215	0.449	0.142	0.057
Operating Cost - Annual - $ (1972)	560	66,500	130,000	57,700	45,000
Value of Recovered Product - $/Yr.	0	0		0	0
Net Operating Cost - $/lb.	0.0014	0.166	0.419	0.186	0.067
Efficiency - % - SF	100	100	99.9	100	100
Efficiency - % - SFRK	100	100	99.9	100	100

*Profit of $0.97/lb. Isocyanate from sale of HCl

TABLE TDI-IV
CATALOG OF EMISSION CONTROL DEVICES
ISOCYANATES

Page 2 of 3

ABSORBER/SCRUBBERS

EPA Code No. for plant using	17-3	17-4	17-9	17-9	17-6
Flow Diagram (Fig. TDI-1) Stream I. D.	E	F	I		F
Device I. D. No.	F-1	F-102	F-101		F-102
Control Emission of	Phosgene	Reactor Gas	HCl & Phosgene	Aniline	Amines
Scrubbing/Absorbing Liquid	10% Caustic	10% NaOH	10% Caustic	Water	N. A.
Type - Spray			(2)	X	Condenser
Packed Column	X	X	X		
Tray Column			X		
Scrubbing/Absorbing Liquid Rate - GPM	400	100	3000 1500		N. A.
Design Temperature (Operating Temperature) - F°	150	Ambient	Ambient Ambient (140) (140)	110	300°
Gas Rate - SCFM (lb./Hr.)	200	13		100 - 133	78
T-T Height, Ft.	42 (ea)	30	22 32	9	N. A.
Diameter - Ft.	2 in series 7	2	7 7	2	N. A.
Washed Gases to Stack	Yes	No - to sump	Yes Yes	Yes	No - to sump
Stack Height - Ft.	42	Ground	Ground	50	Ground
Stack Diameter - In.	84	8 ft.	10	6	3' x 5'
Installed Cost Mat'l. & Labor - $	92,905	34,700	1,122,000	2000	9600
Installed Cost Based on "Year" - $	1972	1969 - 1971	1966 - 1970	1966 - 1970	1970
Installed Cost - ¢/lb. Isocyanate	0.139	0.13	0.66	0.001	0.024
Operating Cost - Annual - $ (1972)	99,000	41,900	218,000	1000	1200
Value of Recovered Product - $/Yr	0	0	0	0	0
Net Operating Cost - ¢/lb.	0.148	0.16	0.128	0.0006	0.003
Efficiency - % - ST	100	100	99.94	99.94	100
Efficiency - % - SKRP	100	100	99.94	99.94	100

ABSORBER/SCRUBBERS

EPA Code No. for plant using	17-6	17-6	17-7	17-10	17-10
Flow Diagram (Fig. TDI-1) Stream I. D.	E	F	F	E	I
Device I. D. No.	F-101	F-101	F-101	F-101	F-105
Control Emission of	Phosgene	CO and Phosgene	Phosgene	Phosgene	HCl
Scrubbing/Absorbing Liquid	8% NaOH	10% Caustic	18% Caustic	20% Caustic	Limestone
Type - Spray		(3)	(4)		Limestone Absorbing Pit
Packed Column	X	X	X	X	
Tray Column					
Scrubbing/Absorbing Liquid Rate - GPM	50	25 1800	1900 1200	300	4226 PPH Limestone
Design Temperature (Operating Temperature) - F°	140	104 102	Ambient Ambient	113	Ambient
Gas Rate - SCFM (lb./Hr.)	65	109 ?	5000 5000	(700 - 1000)	2945
T-T Height, Ft.	25.5	53.5 57.7	38.3 27.7	16, 20	2'
Diameter - Ft.	2	2 7	7 7	3 , 9	15' x 15'
Washed Gases to Stack	No	No Yes	Yes Yes	No	Yes
Stack Height - Ft.		130	160 160		20
Stack Diameter - In.		12	30 30		10
Installed Cost Mat'l. & Labor - $	88,481	655,245	567,000	240,000	200,000
Installed Cost Based on "Year" - $	1969 - 1970	1965 - 1971	1971	1965	1963 - 1965
Installed Cost - ¢/lb. Isocyanate	0.22	1.64	0.56	0.40	0.33
Operating Cost - Annual - $ (1972)	6620	239,750	241,600	185,000	211,000
Value of Recovered Product - $/Yr	0	0	0	0	0
Net Operating Cost - ¢/lb.	0.016	0.60	0.23	0.31	0.351
Efficiency - % - ST	100	$COCl_2$ 100, Toluene 0	99+	HCl 51.4, $COCl_2$ 73.4	99.7
Efficiency - % - SKRP	98.1	78.2	88.1	66	99.7

TABLE [illegible]

CATALOG OF EMISSION CONTROL DEVICES

ISOCYANATES

Page 3 of 3

INCINERATION AND [illegible] DEVICES					
EPA Code No. for plant using	17-[illegible]	17-6	17-7	17-8	17-10
Flow Diagram (Fig. [illegible]) Stream I.D. [illegible]	[illegible]	A	A	[illegible]	A
Device I.D. No.	F-103	F-106	F-106 (3)	F-103	F-104
Type of Compound Incinerated	Heavy Isocyanate Residuals	Ethanol and H_2	CO and Phosgene	Heavy Isocyanate Residuals	Phosgene Decomp. Off-Gas
Type of Device	Pot Incinerator	Flare	Dilution Stack	Incinerator	Flare
Material Incinerated, lb/hr (Design)	[illegible]	120	(5000)	8300	1000
Auxiliary Fuel Req'd (excl. pilot)			None		
Type		Gas		Nat. Gas	None
Rate - [illegible]		1.25 MM [illegible]			
Device or Stack Height - [illegible]	Ground [illegible]	[illegible]	160	No Data	110'
Installed Cost - [illegible]	[illegible]	332,019	(1)	No Data	3500*
Installed Cost based on "Year" [illegible]	19[illegible]	1966	(1)	No Data	1963
Installed Cost - [illegible] Isocyanate [illegible]	0.0[illegible]	0.03	(1)	No Data	0.00[illegible]
Operating Cost - Annual [illegible]	[illegible]	9,360	(1)	No Data	600*
Operating Cost - [illegible]	0.02	0.023	(1)	No Data	0.001
Efficiency - [illegible]	100	100	0 (2)	No Data	100
Efficiency - [illegible]	100	100	0 (2)	No Data	9.3

*Prorated [illegible] of total [illegible] [illegible] flare also
(1) See plant [illegible] scrubbers [illegible] device [illegible] Cost for dilution stacks included there
(2) [illegible] and [illegible] does nothing to remove them from this stream
(3) [illegible] personnel protection in the [illegible]

EXPLANATION OF NOTES
TABLE TDI-IV
CATALOG OF EMISSION CONTROL DEVICES
ISOCYANATES

1. One column of two different diameters, packed with pall rings.

2. Two sets of two columns in series. Flow evenly split between the two sets. Costs are for entire system.

3. Two columns in series. Part of the gas flows thru both columns, the rest goes to the second column only.

4. Two columns and stacks in parallel. Costs are for both systems.

TABLE TDI-V
NUMBER OF NEW PLANTS BY 1980

Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
1088	0	1088	1800	2120	1032	100	10

NOTE:

All capacities in millions of lbs./year.

TABLE TDI-VI
EMISSION SOURCE SUMMARY
TON/TON ISOCYANATE

Emission	Source					Total
	Phosgene Decomposer	Isocyanate Scrubber Vent	Residual Gas Scrubber Vent	Miscellaneous Vents	Plant Flare	
Hydrocarbons	0.001134	0.000032	0.000015	TR	0	0.001181
Particulates & Aerosols	0.000033	0.000014	TR	0.000383	0.000249	0.000679
NO_x	0	0	0	0	0	0
SO_x	0	0	0.000015	0	0	0.000015
CO	0.004298	0.001159	0.077237	0	0	0.082694

TABLE TDI-VII
WEIGHTED EMISSION RATES

Chemical Isocyanates

Process Phosgenation

Increased Capacity by 1980 1032 MM Lbs./Year

Pollutant	Emissions Lb./Lb.	Increased Emissions MM Lbs./Year	Weighting Factor	Weighted Emissions MM Lbs./Year
Hydrocarbons	0.001181	1.22	80	97.6
Aerosols	0.000679	0.700	60	42.0
NO_x	0	0	40	0.0
SO_x	0.000015	0.015	20	0.3
CO	0.082694	85.3	1	85.3

Significant Emission Index = 225.2

APPENDIX I

FINAL ADDRESS LIST

Air Products & Chemicals, Inc.
P. O. Box 97
Calvert City, Kentucky

Attention: Mr. Howard Watson

Allied Chemical Corp.
Morristown, New Jersey

Attention: Mr. A. J. VonFrank
Director Air & Water
Pollution Control

American Chemical Corp.
2112 E. 223rd
Long Beach, California 90810

Attention: Mr. H. J. Kandel

American Cyanamid Company
Bound Brook, New Jersey

Attention: Mr. R. Phelps

American Enka Corporation
Enka, North Carolina 28728

Attention: Mr. Bennet

American Synthetic Rubber Corp.
Box 360
Louisville, Kentucky 40201

Attention: Mr. H. W. Cable

Amoco Chemicals Corporation
130 E. Randolph Drive
Chicago, Illinois

Attention: Mr. H. M. Brennan, Director
of Environomental Control Div.

Ashland Oil Inc.
1409 Winchester Ave.
Ashland, Kentucky 41101

Attention: Mr. O. J. Zandona

Borden Chemical Co.
50 W. Broad Street
Columbus, Ohio 43215

Attention: Mr. Henry Schmidt

Celanese Chemical Company
Box 9077
Corpus Christi, Texas 78408

Attention: Mr. R. H. Maurer

Chemplex Company
3100 Gulf Road
Rolling Meadows, Illinois 60008

Attention: Mr. P. Jarrat

Chevron Chemical Company
200 Bush Street
San Francisco, California 94104

Attention: Mr. W. G. Toland

Cities Service Inc.
70 Pine Street
New York City, NY 10005

Attention: Mr. C. P. Goforth

Clark Chemical Corporation
Blue Island Refinery
131 Kedzie Avenue
Blue Island, Illinois

Attention: Mr. R. Bruggink, Director
of Environmental Control

Columbia Nitrogen Corporation
Box 1483
Augusta, Georgia 30903

Attention: Mr. T. F. Champion

Continental Chemical Co.
Park 80 Plaza East
Saddlebrook, NJ 07662

Attention: Mr. J. D. Burns

Cosden Oil & Chemical Co.
Box 1311
Big Spring, Texas 79720

Attention: Mr. W. Gibson

Dart Industries, Inc.
P. O. Box 3157
Terminal Annex
Los Angeles, California 90051

Attention: Mr. R. M. Knight
Pres. Chemical Group

Diamond Plastics
P. O. Box 666
Paramount, California 70723

Attention: Mr. Ben Wadsworth

Diamond Shamrock Chem. Co.
International Division
Union Commerce Building
Cleveland, Ohio 44115

Attention: Mr. W. P. Taylor, Manager
Environ. Control Engineering

Dow Badische Company
Williamsburg, Virginia 23185

Attention: Mr. L. D. Hoblit

Dow Chemical Co. - USA
2020 Building
Abbott Road Center
Midland, Michigan 48640

Attention: Mr. C. E. Otis
Environmental Affairs Div.

E. I. DuPont de Nemours & Co.
Louviers Building
Wilmington, Delaware 19898

Attention: Mr. W. R. Chalker
Marketing Services Dept.

Eastman Chemicals Products, Inc.
Kingsport, Tennessee

Attention: Mr. J. A. Mitchell
Executive Vice President
Manufacturing

El Paso Products Company
Box 3986
Odessa, Texas 79760

Attention: Mr. N. Wright,
Utility and Pollution
Control Department

Enjay Chemical Company
1333 W. Loop South
Houston, Texas

Attention: Mr. T. H. Rhodes

Escambia Chemical Corporation
P. O. Box 467
Pensacola, Florida

Attention: Mr. A. K. McMillan

Ethyl Corporation
P. O. Box 341
Baton Rouge, Louisiana 70821

Attention: Mr. J. H. Huguet

Fibre Industries Inc.
P. O. Box 1749
Greenville, South Carolina 29602

Attention: Mr. Betts

Firestone Plastics Company
Box 699
Pottstown, Pennsylvania 19464

Attention: Mr. C. J. Kleinart

Firestone Synthetic Rubber Co.
381 W. Wilbeth Road
Akron, Ohio 44301

Attention: Mr. R. Pikna

Firestone Plastics Company
Hopewell, Virginia

Attention: Mr. J. Spohn

FMC - Allied Corporation
P. O. Box 8127
South Charleston, W. VA 25303

Attention: Mr. E. E. Sutton

FMC Corporation
1617 J.F.K. Boulevard
Philadelphia, PA

Attention: Mr. R. C. Tower

Foster Grant Co., Inc.
289 Main Street
Ledminster, Mass. 01453

Attention. Mr. W. Mason

G.A.F. Corporation
140 W. 51st Street
New York, NY 10020

Attention: Mr. T. A. Dent, V.P.
of Engineering

General Tire & Rubber Company
1 General Street
Akron, Ohio 44309

Attention: Mr. R. W. Laundrie

Georgia-Pacific Company
900 S.W. 5th Avenue
Portland, Oregan 97204

Attention: Mr. V. Tretter
Sr. Environmental Eng.

Getty Oil Company
Delaware City, Delaware 19706

Attention: Mr. Gordon C. Gaddis

B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, Ohio 44131

Attention: Mr. W. Bixby

Goodyear Tire & Rubber Co.
1144 E. Market Street
Akron, Ohio 44316

Attention: Mr. B. C. Johnson, Manager
Environmental Engineering

Great American Chemical Company
650 Water Street
Fitchburg, Mass.

Attention: Dr. Fuhrman

Gulf Oil Corporation
Box 1166
Pittsburgh, Pennsylvania

Attention: Mr. D. L. Matthews
Vice President -
Chemicals Department

Hercules Incorporated
910 Market Street
Wilmington, Delaware

Attention: Dr. R. E. Chaddock

Hooker Chemical Corporation
1515 Summer Street
Stamford, Conn. 06905

Attention: Mr. J. Wilkenfeld

Houston Chemical Company
Box 3785
Beaumont, Texas 77704

Attention: Mr. J. J. McGovern

Hystron Fibers Division
American Hoechst Corporation
P. O. Box 5887
Spartensburg, SC 29301

Attention: Dr. Foerster

Jefferson Chemical Company
Box 53300
Houston, Texas 77052

Attention: Mr. M. A. Herring

Koch Chemical Company
N. Esperson Building
Houston, Texas 77002

Attention: Mr. R. E. Lee

Koppers Company
1528 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. D. L. Einon

Marbon Division
Borg-Warner Corporation
Carville, Louisiana 70721

Attention: Mr. J. M. Black

Mobay Chemical Corporation
Parkway West & Rte 22-30
Pittsburgh, Pennsylvania 15205

Attention: Mr. Gene Powers

Mobil Chemical Company
150 E. 42nd Street
New York, NY 10017

Attention: Mr. W. J. Rosenbloom

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Attention: Mr. J. Depp, Director of
Corp. Engineering

National Distillers & Chem. Corp.
U.S. Industrial Chem. Co. Div.
99 Park Avenue
New York, NY 10016

Attention: Mr. J. G. Couch

National Starch & Chem. Co.
1700 W. Front Street
Plainfield, New Jersey 07063

Attention: Mr. Schlass

Northern Petrochemical Company
2350 E. Devon Avenue
Des Plaines, Illinois 60018

Attention: Mr. N. Wacks

Novamont Corporation
Neal Works
P. O. Box 189
Kenova, W. Virginia 25530

Attention: Mr. Fletcher

Olin Corporation
120 Long Ridge Road
Stamford, Conn.

Attention: Mr. C. L. Knowles

Pantasote Corporation
26 Jefferson Street
Passaic, New Jeresy

Attention: Mr. R. Vath

Pennwalt Corporation
Pennwalt Building
3 Parkway
Philadelphia, PA 19102

Attention: Mr. J. McWhirter

Petro-Tex Chemical Corporation
Box 2584
Houston, Texas 77001

Attention: Mr. R. Pruessner

Phillips Petroleum Co.
10 - Phillips Bldg.
Bartlesville, Oklahoma 74004

Attention: Mr. B. F. Ballard

Polymer Corporation, Ltd.
S. Vidal Street
Sarnia, Ontario
Canada

Attention: Mr. J. H. Langstaff
General Manager
Latex Division

Polyvinyl Chemicals Inc.
730 Main Street
Wilmington, Mass. 01887

Attention: Mr. S. Feldman, Director of
Manufacturing - Engineering

PPG Industries Inc.
One-Gateway Center
Pittsburgh, Pennsylvania 15222

Attention: Mr. Z. G. Bell

Reichold Chemicals Inc.
601-707 Woodward Hts. Bldg.
Detroit, Michigan 48220

Attention: Mr. S. Hewett

Rohm & Haas
Independence Mall West
Philadelphia, PA 19105

Attention: Mr. D. W. Kenny

Shell Chemical Co.
2525 Muirworth Drive
Houston, Texas 77025

Attention: Dr. R.L. Maycock
Environ. Eng. Div.

Sinclair-Koppers Chem. Co.
901 Koppers Building
Pittsburgh, Pennsylvania 15219

Attention: Mr. R. C. Smith

Skelly Oil Company
Box 1121
El Dorado, Kansas 67042

Attention: Mr. R. B. Miller

Standard Brands Chem. Industries
Drawer K
Dover, Delaware 19901

Attention: Mr. E. Gienger, Pres.

Stauffer Chemical Co.
Westport, Connecticut

Attention: Mr. E. L. Conant

Stepan Chemical Company
Edens & Winnetka Road
Northfield, Illinois 60093

Attention: Mr. F. Q. Stepan
V.P. - Industrial Chemicals

Tenneco Chemicals Inc.
Park 80 Plaza - West 1
Saddlebrook, NJ 07662

Attention: Mr. W. P. Anderson

Texas - U.S. Chemical Company
Box 667
Port Neches, Texas 77651

Attention: Mr. H. R. Norsworth

Thompson Plastics
Assonet, Mass. 02702

Attention: Mr. S. Cupach

Union Carbide Corporation
Box 8361
South Charleston, W. Virginia 25303

Attention: Mr. G. J. Hanks, Manager
Environ. Protection
Chem. & Plastics Division

Uniroyal Incorporated
Oxford Management &
Research Center
Middlebury, Conn. 06749

Attention: Mr. F. N. Taff

The Upjohn Company
P. O. Box 685
La Porte, Texas

Attention: Mr. E. D. Ike

USS Chemicals Division
U.S. Steel Corporation
Pittsburgh, Pennsylvania 15230

Attention: Mr. Gradon Willard

W. R. Grace & Company
3 Hanover SquarNew York, NY 10004

Attention: Mr. Robt. Goodall

Wright Chemical Corporation
Acme Station
Briegelwood, North Carolina 28456

Attention: Mr. R. B. Catlett

Wyandotte Chemical Corp.
Wyandotte, Michigan 48192

Attention: Mr. John R. Hunter

Vulcan Materials Company
Chemicals Division
P.O. Box 545
Wichita, Kansas 67201

Attention: H.M. Campbell
Vice-President, Production

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs
Research Triangle Park, North Carolina 27711

Dear Sir:

The Environmental Protection Agency, Office of Air Programs is engaged in a study of atmospheric emissions from the Petrochemical Industry. The primary purpose of this study is to gather information that will be used to develop New Stationary Source Performance Standards which are defined in Section 111 of the Clean Air Act as amended December 31, 1970 (Public Law 91604). These new source standards will not be set as part of this study but will be based (to a large extent) on the data collected during this study.

A substantial part of the work required for this study will be performed under contract by the Houdry Division of Air Products and Chemicals. Several other companies not yet chosen will assist in the source sampling phase of the work.

Very little has been published on atmospheric emissions from the petrochemical industry. The first part of this study will therefore rank the most important petrochemical processes in their order of importance in regard to atmospheric emissions. The Petrochemical Emissions Survey Questionnaire will be the primary source of data during the first phase. This ranking will be based on the amount and type of emissions from the process, the number of similar processes and the expected growth of the process. A second in-depth phase of the study to document emissions more completely will be based on information obtained through actual stack sampling.

Attached you will find a copy of the petrochemical questionnaire which you are requested to complete and return to the Enviromental Protection Agency within forty-two (42) calender days.

You are required by Section 114 of the Clean Air Act to complete each applicable part of this questionnaire except for question II.4. and II.5. These two questions are concerned with the water and solid waste generated by the process itself not with that generated by the emission control equipment. This information would be of a value to the EPA and your answers will be appreciated.

This questionnaire is to be completed using the information presently available to your company. We are not asking that you perform special non-routine measurements of emissions streams. We are asking for results of measurements that you have made or for estimates when measurements have not been made. Where requested information is not available, please mark sections "not available". Where the requested information is not applicable to the subject process, mark the questionnaire sections "not applicable". A sample questionnaire, filled out for a fictitious process is enclosed for your guidance.

It is the opinion of this office that for most processes it should be possible to answer all survey questions without revealing any confidential information or trade secrets. However, if you believe that any of the information that we request would reveal a trade secret if divulged you should clearly identify such information on the completed questionnaire. Submit, with the completed questionnaire, a written justification explaining the reason for confidential status for each item including any supportive data or legal authority. Forward a duplicate of your claim and supporting material, without the questionnaire data, to our counsel, Mr. Robert Baum, Assistant General Counsel, Air Quality and Radiation Division, Environmental Protection Agency, Room 17B41, 5600 Fishers Lane, Rockville, Maryland 20852. Emission data cannot be considered confidential.

Final authority for determining the status of the information resides with the Enviromental Protection Agency. A reply describing the decision reached will be made as soon as possible after receipt of the claim and supporting information. During the period before the final determination this office will honor any request to treat the questionnaire information as confidential.

Information declared to be a trade secret is subject to protection from being published, divulged, disclosed or made known in any manner or to any extent by Section 1905 of Title 18 of the United States Code. The disclosure of such information, except as authorized by law, shall result in a fine of not more than $1,000 or imprisonment of not more than one year, or both; and shall result in removal of the individual from his office or employment.

Although it should be noted that Section 114, Subsection C of the Clean Air Act allows such information to be disclosed "to other officers, employees, or authorized representatives of the United States concerned with carrying out the Act or when relevant in any proceeding under this Act," no confidential information will be revealed to any private concern employed by the Environmental Protection Agency to assist in this study.

The handling and storage of information for which the determination is pending or information which has been determined to be of a confidential nature is carefully controlled. Preliminary control procedures require that the material be labeled confidential and stored in a locked file.

The complete form should be mailed to:

Mr. Leslie B. Evans
Environmental Protection Agency
Office of Air Programs
Applied Technology Division
Research Triangle Park, NC 27711

It is possible that additional copies of this questionnaire which will request information covering other petrochemical processes or other plants using the same process and operated by your organization will be sent to you in the course of this study. Clarification of items contained in the questionnaire may be obtained from Mr. Evans by telephone at 919/688-8146. Thank your for your help in this matter.

Sincerely,

Leslie B. Evans

Leslie B. Evans
Industrial Studies Branch

Petrochemical Questionnaire

Instructions

I. Capacity. Describe capacity of process by providing the following:

1. Process capacity. Give capacity in units per year and units per hour. An "actual" capacity is preferred but "published" or "name plate" capacity will be satisfactory if such capacity is reasonably correct. Do not give production.

2. Seasonal variation. Describe any significant seasonal variations in production.

As example an ammonia plant might produce more during spring and winter quarters:

quarter	Jan-Mar	April-June	July-Sept	Oct-Dec	Year Total
%	40	20	10	30	100%

II. Process. Describe the process used to manufacture the subject chemical by providing the following:

1. Process name. If the process has a common name or description, give this. If any portion of the process (e.g., product recovery method) has a common name, give this.

2. Block Diagram. Provide a block diagram of the process showing the major process steps and stream flows.

(a) Show on block diagram all streams described below. Identify each required stream by letter. (A,B,C, etc.) In general the streams that must be identified are (1) the gaseous emissions streams before and after any control device and (2) the gaseous or liquid streams which, after leaving the process site, produce gaseous emissions during further processing or combustion.

(i) Any gaseous waste streams before and after any pollution device should be shown and identified.

(ii) Streams from rupture disks or pressure relief valves which protect equipment from operating upsets but discharges less than once every year need not be shown.

(iii) Emissions from pressure relief systems that normally discharge during power failures or other emergencies should be shown, identified by letter and labeled "emergency".

(iv) Emissions from fueled heaters such as "heat transfer medium" heaters, steam generators, or cracking furnaces need not be shown if they are fueled completely by fuels listed in Question VII and are not used to incinerate by-products or off gases.

(v) Emissions from Claus units associated with process need not be shown. Stream to Claus unit should be shown and identified with letter.

(vi) Emissions from a central power plant (or steam plant) which burns a liquid fuel produced as a by-product of this process need not be shown. Such liquid fuel should be shown and identified by letter.

(vii) Emissions from a central power plant (or steam plant) which burns a gaseous fuel produced as a by-product of this process need not be shown. Such gaseous fuel should be shown and identified by letter.

(b) Show all gaseous emission control devices. Identify each control device on the block diagram by a three digit number (101, 102, 103, etc.)

(c) Show all stacks or vents that vent streams listed in (a) and (b) above. It a stack to vent discharges emissions from more than one source, label this stack or vent with a letter in sequence started in II.2.a. (D,E,F, etc.) If a stack or vent discharges emissions from only one source label the stack with the same letter as the emission stream.

3. Raw material and product. Give approximate chemical composition and approximate amount (on yearly basis and at capacity given in I.1) of all raw-materials, products and by-products. If composition or amounts vary, give ranges. Composition may be given in commonly accepted terms when a chemical analysis would be inappropriate. The description "light straight-run naphtha" would be adequate.

4. Waste water. Is there a waste water discharge from this process which is (eventually) discharged to a receiving body of water? Is this waste water treated by you or by others? Give the approximate volume and indicate whether this is measured or estimated.

5. Waste solids. Is there a waste solids discharge from this process? How is it disposed of? Give the approximate daily total of waste solids and indicate if this is measured or estimated.

III. Emissions (composition and flow): For each stream requested in II.2.a. and shown on the block diagram by letter provide the following: (Use separate sheets for each identified location - 6 copies are provided). All of the questions will not be applicable for each stream.

As an example, question 10, odor problem, applies only to streams which are emitted to the atmosphere.

1. Chemical composition and flow. Give composition as completely as possible from information you have available. Do not omit trace constituents if they are known. If anything (e.g. fuel) is added upstream of any emission control devices, give the chemical composition and flow prior to the addition, and give the quantity and composition of the added material. If liquids or solids are present (in gas stream) provide the composition and amount of these also. Give flow volume (SCFM), temperature (F°) and pressure (psig or inches H_2O).

2. Variation in chemical composition and flow. If average stream composition or flow varies significantly over some period of time during normal or abnormal operation, discuss this variation and its frequency. Relate this to the average and range of composition given in III.1.

   As examples:

   "During start-up (once a month) the benzene is about 12% by volume for one hour" or "the benzene can be expected to go from 5% to 9% by volume during life of catalyst, the 'average' figure given is about average over the catalyst life" or "power failures occur about once each winter causing stream A to increase from 0 to (initially) 50,000 lbs/hr., and about 8,000 lbs is vented over a 15 minute period."

3. Production rate during sampling. If stream composition and volume flow rates given in answer to questions III.1. and III.2. were measured at a plant production rate different than the capacity of the plant given in I.1. give the rate at which the measurements were made.

   As example:

   Figures given for this stream (A) were made when plant was operating at 90% of capacity given in I.1.

4. Methods used to determine composition and flow. Is information from material balance, from sample and analysis, or other? Describe briefly.

5. Sampling procedure. If samples have been taken, give summary description of sampling procedure or give reference if described in open literature.

6. Analytical procedure. If samples have been taken, give summary description of analytical procedure or give reference if described in open literature.

7. Sampling frequency. How often is the stream sampled?

   As Examples:

   "continuous monitor" or "twice a shift for last 18 months" or "once in the fall of 1943".

8. Confidence level. Give some idea how confident you are in regard to compositions in III.1.

   As examples:

   "probably correct ± 20%" or "slightly better than wild guess".

9. Ease of sampling. How difficult is it to sample this stream?

   As examples:

   "sample line runs into control room" or "sample port provided but accessible only with 20-ft. ladder."

10. Odor problem. Is the odor of this emission detectable at ground level on the plant property or off the plant property? If odors carry beyond the plant property are they detectable frequently or infrequently? Have you received a community odor complaint traceable to this source in the past year? Has the odorous material been chemically identified? What is it?

IV. Emission control device. Supply the following information for each control device shown on the block diagram. (Use separate sheets for each - 3 copies are provided).

1. Engineering description. Give brief description and process sketch of the control device. Attach print or other description if you prefer. Show utilities used, steam produced, product recovered, etc. Give manufacturer, model number and size (if applicable). Give complete (applicable) operating conditions, i.e. flows, temperatures, pressure drops, etc.

2. Capital cost of emission control system.

   (a) Give capital cost for the emission control device as it is described in IV.1. above; i.e., if equipment has been modified or rebuilt give your best estimate of capital cost of equipment now in service. For the total installed cost give the approximate breakdown by year in which cost was incurred.

   As example:

   Major equipment cost $155,000
   Total installed cost $250,000

Year	Cost
1963	$160,000
1964	40,000
1971	50,000
	$250,000

   (b) On the check list given mark whether the items listed are included in total cost as given above. Give one sentence explanation when required but do not give dollar amounts.

   (c) Was outside engineering contractor used and was cost included in capital cost?

   (d) Was in-house engineering used and was cost included in capital cost?

   (e) Was emission control equipment installed when plant was built?

3. Operating cost of emission control system. Give the best estimate of cost of operating emission control system in dollars per year with process operated at capacity given in I.1. Other disposal (g) would include, as example, the cost of incinerating a by-product stream which has no value.

V. Stack or vent description. Each stack or vent should have been identified by letter on the block diagram. Provide the requested information for each stack. Stack flow, V.4. should be entered only when it is not possible to calculate this number by adding gas flows given in III.1.

An example would be when an off gas from the process is discharged into a power plant stack.

VI. Tankage. Give information requested for all tankage larger than 20,000 gallons associated with the process and normally held at atmospheric pressure (include raw material, process, product and by-product tankage). Method of vapor conservation (3.) might include, as examples:

"none, tank vents to air"
"floating roof"
"vapor recovery by compression and absorption".

VII. Fuels. If fuels are used in the process give the amount used on a yearly basis at capacity given in I.1. Do not include fuel used in steam power plants. Give sulfur content. Identify each fuel as to its source (natural gas pipeline, process waste stream, Pennsylvania soft coal). Is the fuel used only as a heat source (as with in-line burner)?

VIII. Other emissions. If there is a loss of a volatile material from the plants through system leaks, valve stems, safety valves, pump seals, line blowing, etc., this loss is an emission. In a large complex high pressure process this loss may be several percent of the product. Has this loss been determined by material balance or other method? What is it? Give best estimate.

IX. Future plans. Describe, in a paragraph, your program for the future installation of air pollution control equipment for this unit or for future improvements in the process which will reduce emissions.

OMB Approval Number 158 S 72019

This example questionnaire has been completed for a fictitious company and process.

Example Questionnaire

Air Pollution Control Engineering and Cost Study of the Petrochemical Industry

Please read instructions before completing questionnaire.

Subject chemical: Pyrrole

Principal by-products: Pyrrolidone

Parent corporation name: Orivne Petrochemical Co.

Subsidiary name: Noissime Division

Mailing address: P.O. Box 1234
Rianaelc, North Carolina, 27700

Plant name: Rianaelc Plant

Physical location: 30 miles N.W. Durham, North Carolina

(include county and
air quality control
region) Orange County; Eastern Piedmont Intrastate (Region IV)

Person EPA should contact regarding information supplied in this questionnaire

Name: John Doe

Title: Supervisor of Process Development

Mailing address: Noissime Division of O.P.C.
P.O. Box 1234
Rianaelc, North Carolina, 27700

Telephone number: 919 XXX XXXX

Date questionnaire completed: May 30, 1972

I. Capacity.

1. Process capacity. (not production)

80,000,000 lbs. per year

10,000 lbs. per hour

2. Seasonal variation. (of production)

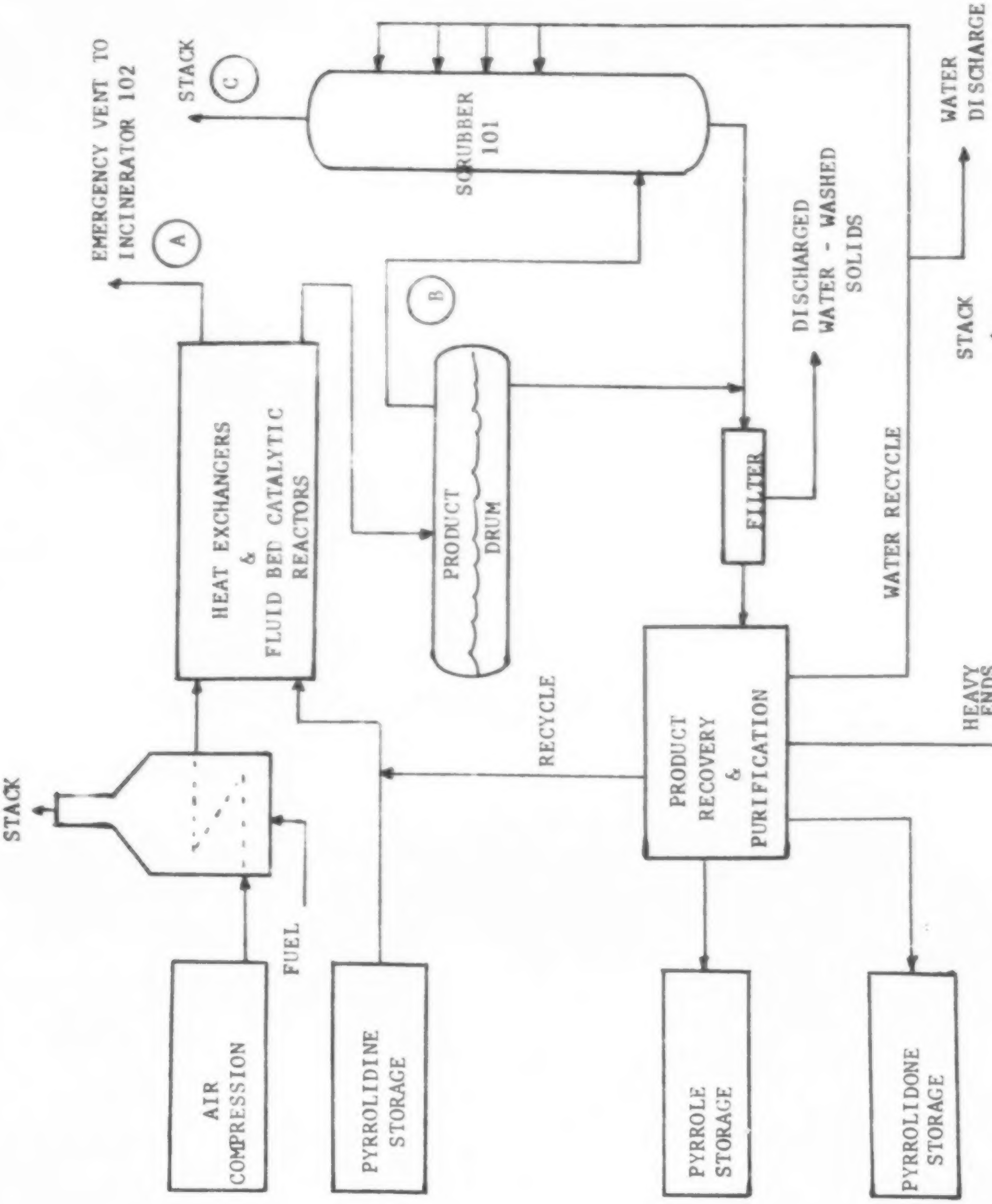
quarter	1	2	3	4	year total
%	30	20	20	30	100%

II. Process.

1. Process name.

Reivrep - Process (oxidative dehydrogenation of pyrrolidine)

2. Block diagram.



EMERGENCY VENT TO INCINERATOR 102
A
STACK
C
SCRUBBER 101
WATER DISCHARGE
DISCHARGED WATER - WASHED SOLIDS
B
STACK
E
HEAT EXCHANGERS & FLUID BED CATALYTIC REACTORS
PRODUCT DRUM
FILTER
WATER RECYCLE
INCINERATOR 102
RECYCLE
HEAVY ENDS
D
PRODUCT RECOVERY & PURIFICATION
STACK
FUEL
AIR COMPRESSION
PYRROLIDINE STORAGE
PYRROLE STORAGE
PYRROLIDONE STORAGE

II. Process. (Continued)

3. Raw materials and products

Raw materials

Name	Quantity	Composition
Pyrrolidine	130,000,000 lbs/yr.	pyrrolidine 98%
		other amines 2%

Product and by-products

Name	Quantity	Composition
Pyrrole	80,000,000 lbs/yr.	pyrrole 99.5%
Pyrrolidone	20,000,000 lbs/yr.	pyrrolidone 99.5%

II. Process. (Continued)

4. Waste water.

750 gal/hr. treated by us, measured in treatment unit.

5. Waste solids.

200 lbs/hr. catalyst dust from filter. Estimated average quantity hauled away by solids waste disposal contractor.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter A.

1. Flow ? Temperature ? Pressure ________.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid		

Depending upon cause of emergency, emissions could range from contaminated feed to contaminated product. Upset durations seldom exceed 15 minutes during which time incinerator operation would be modified. For initial 1-2 minutes after upset pollutants might leave incinerator stack. Following that, stack gases will be nearly 100% CO_2, H_2O & N_2. On average, such upsets occur two or three times per year. Particulates are possible, depending upon cause of upset. One such upset occurred in 1969.

* Particulate matter should be described as fully as possible.________________

III. Continued For stream flow shown on block diagram by letter___A___.

2. Composition variation.

   See III-1

3. Production rate during sampling.

   Never Sampled

4. Method used to determine composition and flow.

   Not applicable

III. Continued For stream flow shown on block diagram by letter A.

5. Sampling procedure.

Not Applicable

6. Analytical procedure.

Not Applicable

7. Sampling frequency.

Never

III. Continued For stream flow shown on block diagram by letter A.

8. Confidence level.

Not Applicable

9. Ease of sampling.

Impossible

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

Not Applicable

III.1. Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter B.

1. Flow 10,000 SCFM Temperature 110°F Pressure 25 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	150 lbs./hour	100-200 lbs./hour
Nitrogen	N_2	Gas	83.8 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amines	**	Vapor	0.1 "	0.05-0.2%
Nitrogen Oxides	NO_x	Gas	300 VPPM	200-500 VPPM

* Particulate matter should be described as fully as possible. Catalyst Dust (composition is proprietary) contains cobalt and chromium on alumina base. 100% less than 15 microns; 60% less than 10 microns; 20% less than 5 microns; 5% less than 1 micron.

** Composition unknown - mixture of feed, products and other amines.

III. Continued For stream flow shown on block diagram by letter B .

2. Composition variation.

During 2nd and 3rd quarter when plant is operated below capacity, nitrogen is at high end of range and all other materials near low end. During start-up or plant upset (average about 50 hours/year) nitrogen is near low end of range and all other materials near high end.

3. Production rate during sampling.

Average composition based on rated capacity.

4. Method used to determine composition and flow.

Engineering calculation and plant material balance (flow). Composition calculated on basis of stream "C" analysis and estimated amine losses prior to installation of scrubber.

III. Continued For stream flow shown on block diagram by letter ___B___.

5. Sampling procedure.

Never sampled.

6. Analytical procedure.

Never Analyzed.

7. Sampling frequency.

See (5) above.

III. Continued For stream flow shown on block diagram by letter B.

8. Confidence level.

± 10%

9. Ease of sampling.

No sample taps are available, but one could be easily installed in readily accessible location. However, it would not be 8 pipe diameters from a disturbance.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

No applicable - this stream is no longer emitted to the atmosphere.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter C.

1. Flow 10,000SCFM Temperature 100°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	10 lbs./hour	5-20 lbs./hour
Nitrogen	N_2	Gas	83.9 Vol. %	80-85%
Oxygen	O_2	Gas	1.4 "	1-2%
Carbon Monoxide	CO	Gas	4.1 "	3-5%
Carbon Dioxide	CO_2	Gas	1.4 "	1-2%
Hydrogen	H_2	Gas	2.1 "	2-2.5%
Water	H_2O	Vapor	7.1 "	6.5-7.5%
Various Amine	**	Vapor	50 YPPMV	30-100 PPMV
Nitrogen Oxides	NO_x	Gas	300 YPPMV	200-500 PPMV

* Particulate matter should be described as fully as possible. See "B". Size distribution 100% less than 5 microns; 60% less than 1 micron.

** See "B".

III. Continued For stream flow shown on block diagram by letter C.

2. Composition variation.

See "B"

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

See "B" for flow. Specific analysis methods are given in III-6(C)

III. Continued For stream flow shown on block diagram by letter C.

5. Sampling procedure.

   a. Particulates and moisture collected in sampling train as detailed in Federal Register, Dec. 23, 1971 (Method 5).

   b. NO_x sampled by EPA Method 7.

   c. Other constituents collected using grab sampling procedures for collection of gas. Sample size 10 liters in stainless steel tank.

6. Analytical procedure.

   a. Particulates and moisture determined gravimetrically as detailed in Federal Register, Dec. 23, 1971. (Method 5)

   b. NO_x determined by EPA method 7.

   c. Hydrogen, oxygen, and nitrogen determined by mass spectrometer analysis at local university.

      Amine, CO and CO_2 determined by infra-red analysis.

7. Sampling frequency.

   Once, - one month after scrubber was put on stream.

III. Continued For stream flow shown on block diagram by letter C.

8. Confidence level.

Oxygen, CO_2, CO and H may be ± 10%.

Nitrogen would be better than this, perhaps ± 5%

Amines are near limit of detection - ± 50%.

9. Ease of sampling.

Difficult - only sample tap is six feet above top of scrubber tower - approximately 65 feet in air - reached by caged ladders.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? [✓ Yes]/no Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently? [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amine compounds.

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter D.

1. Flow 300 GPH Temperature $300^{\circ}F$ Pressure 10 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Heavy Amines	$(CH_x)_yNH_z$	Liquid	100%	

* Particulate matter should be described as fully as possible. Very fine catalyst dust - never sampled or analyzed - estimated to be 1-5 lbs./hour.

III. Continued For stream flow shown on block diagram by letter D.

2. Composition variation.

Not applicable - unknown - never analyzed.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Rotameter in liquid line for flow. Composition unknown.

III. Continued For stream flow shown on block diagram by letter D.

5. Sampling procedure.

Not applicable.

6. Analytical procedure.

Not applicable.

7. Sampling frequency.

Not applicable.

III. Continued For stream flow shown on block diagram by letter D.

8. Confidence level.

Not applicable.

9. Ease of sampling.

Liquid drain line is available at ground level. Could be used for sample tap.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/no Off the plant property? Yes/no If odors carry beyond the plant property are they detectable infrequently? Yes/no Frequently? Yes/no Have you received a community odor complaint traceable to this source in the past year? Yes/no Has the odorous material been chemically identified? Yes/no What is it?____________________

Not applicable - not an emitted stream.

III. 1 Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter E.

1. Flow 10,000SCFM Temperature 450°F Pressure 0 PSIG.

Component Name	Formula	State	Average amount or composition	Composition Range
Particulate	*	Solid	Trace	
Nitrogen	N_2	Gas	77.0 Vol. %	76.5-77.5%
Oxygen	O_2	Gas	9.2 Vol. %	9-9.5%
Carbon Dioxide	CO_2	Gas	6.4 Vol. %	6-7%
Water	H_2O	Vapor	7.4 Vol. %	7-8%
Nitrogen Oxides	NO_x	Gas	150 VPPM	100-300 VPPM

* Particulate matter should be described as fully as possible. See "D"

III. Continued For stream flow shown on block diagram by letter E.

2. Composition variation.

Random variation depending on many variables such as production rate, ambient air temperature and humidity, catalyst age, etc., all within limits shown.

3. Production rate during sampling.

See "B"

4. Method used to determine composition and flow.

Calculation based on incinerator vendor's specifications, guarantees and laboratory tests.

III. Continued For stream flow shown on block diagram by letter ____E____.

5. Sampling procedure.

   Never sampled.

6. Analytical procedure.

   Never analyzed

7. Sampling frequency.

   See (5) above

III. Continued For stream flow shown on block diagram by letter E.

8. Confidence level.

± 10%

9. Ease of sampling.

No sample tap, very hot stream, no access ladders, minimal insulation.

10. Odor problem. (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level on the plant property? Yes/[✓ no] Off the plant property? [✓ Yes]/no If odors carry beyond the plant property are they detectable infrequently?* [✓ Yes]/no Frequently? Yes/[✓ no] Have you received a community odor complaint traceable to this source in the past year? Yes/[✓ no] Has the odorous material been chemically identified? [✓ Yes]/no What is it? Amines

* Only during start-up or upset of the incinerator and then only if atmospheric conditions are favorable for ground level detection.

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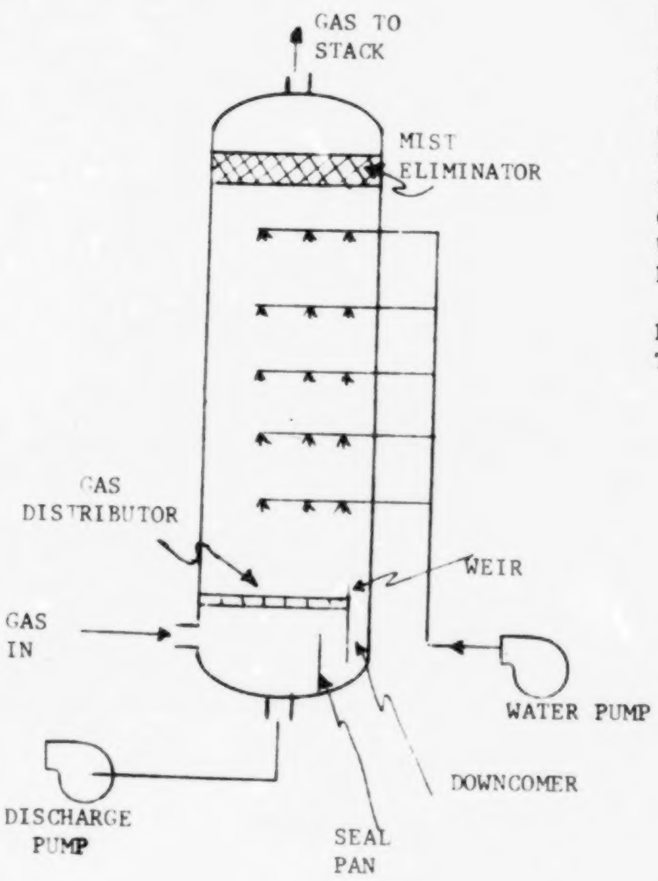
IV. Emission control device

For device shown on block diagram by number 101.

1. Engineering description.


GAS TO STACK
MIST ELIMINATOR
GAS DISTRIBUTOR
WEIR
GAS IN
WATER PUMP
DOWNCOMER
DISCHARGE PUMP
SEAL PAN

Multi-nozzle spray tower manufactured by Rebburcs Corp.
Model No. 10,000-W
Water rate: 100 GPM
Gas rate: 10,000 SCFM
Temperature: 100°F.
Pressure: Atmospheric
Gas AP: 8 in, H_2O
Water Pump Head: 150 Ft.
Discharge Pump Head: 100 Ft.

Diameter of Tower: 6 Ft.
T-T Length: 60 Ft.

Utilities:

35 HP for Pumps

10,000,000 BTU/Hr. Additional steam in product recovery section.

1500 GPM Additional cooling water circulation in product recovery section.

IV. Continued For device shown on block diagram by number 101.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 160,000

Total installed cost $ 350,000

Year	Cost
1968	$350,000

IV. Continued For device shown on block diagram by number 101.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Additional foundation required for scrubber.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
	X	Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 101 .

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
X		Was in-house engineering used?
	X	Was cost included in capital cost?
	X	Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 68,000
(b)	Chemicals *	10,000
(c)	Labor (No Additional Operators)	-
(d)	Maintenance (labor & materials)	14,000
(e)	Water treatment (cost of treating any waste water produced by this control system) **	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	20,000
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT	(89,000)
	Total operating costs	$ 23,000

* Additional cooling water treatment included in utility costs - this cost is for corrosion inhibition in scrubber.

** Water waste is produced by process. It is treated at cost of $30,000/year. This treatment was required before scrubber was installed.

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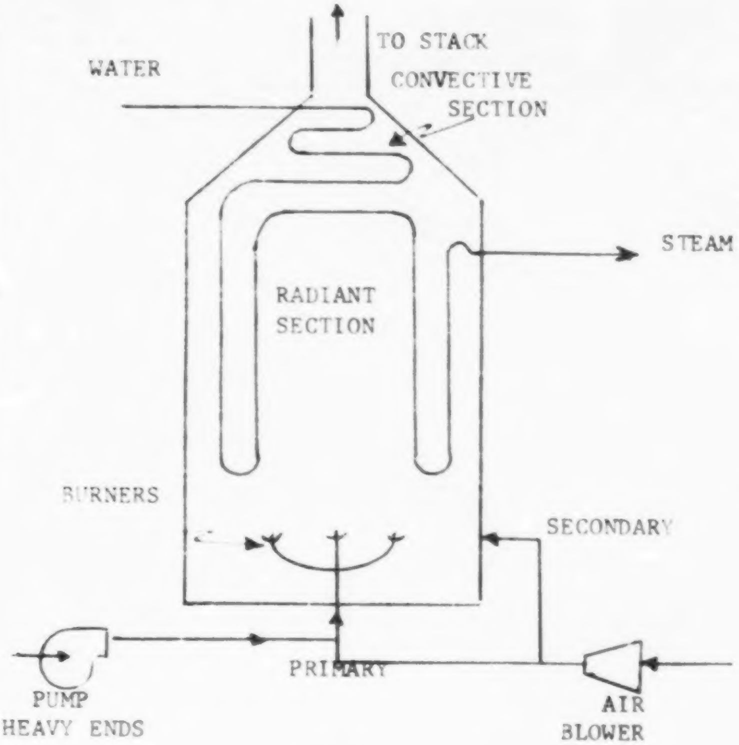
this section.

IV. Emission control device

For device shown on block diagram by number 102.

1. Engineering description.


TO STACK
WATER
CONVECTIVE SECTION
STEAM
RADIANT SECTION
BURNERS
SECONDARY
PRIMARY
PUMP
HEAVY ENDS
AIR
BLOWER

Steam Generator/Waste Incinerator

Manufactured by: Xoberif Corp.
Model No.: 40-H
Heavy Ends Rate: 300 GPH
Air Rate: 9,500 SCFM
Steam Rate: 20,000 lbs./hour
Vessel Diameter: 15 Ft.
Height: 40 Ft.
Tube Diameter: 3 in. nominal
Tube Length: (Material)
Convective (mild steel): 6,000 Ft.
Radiant (304 stainless): 2,000 Ft.

Utilities:

Heavy Ends Pump: 20 HP

Blower: 100 HP

IV. Continued For device shown on block diagram by number 102.

2. Capital cost of emission control system.

(a) Capital cost

Major equipment cost $ 350,000

Total installed cost $ 1,000,000

Year	Cost
1960	$1,000,000

IV. Continued For device shown on block diagram by number 101.

(b) Check list. Mark whether items listed are included in total cost included in IV.2.a. Do not give dollar value -

Yes	No	Cost	Explanation
X		Site development	Additional foundation required for scrubber.
	X	Buildings	
	X	Laboratory equipment	
X		Stack	
X		Rigging etc.	
X		Piping	
X		Insulation	
X		Instruments	
	X	Instrument panels	
X		Electrical	
	X	Facilities outside battery limits*	
	X	Storage tanks, spheres drums, bins, silos	
	X	Catalysts	
	X	Spare parts and non-installed parts	

*Such as - process pipe lines such as steam, condensate, water, gas, fuel, air, fire, instrument and electric lines.

IV. Continued For device shown on block diagram by number 102.

Yes	No	
X		Was outside engineering contractor used?
X		Was cost included in capital cost?
	X	Was in-house engineering used?
X		Was cost included in capital cost?
X		Was emission control equipment installed and constructed at the time plant (process) was constructed?

3. Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)	Utilities	$ 5,000
(b)	Chemicals	-
(c)	Labor (½ man per shift - excludes supervision & overhead)	7,000
(d)	Maintenance (labor & materials)	40,000
(e)	Water treatment (cost of treating any waste water produced by this control system)	-
(f)	Solids remmoval (cost of removing any waste solids produced by this control system)	-
(g)	Other disposal	-
(h)	By-product or product recovery CREDIT- STEAM	($100,000)
	Total operating **credit**	$ 48,000

V. Stack or vent description.

For stack or vent shown on block diagram by letter C.

1. Stack height 100 ft
2. Stack diameter 2 ft
3. Gas temperature stack exit 100 °F
4. Stack flow * SCFM(70°F & 1 Atm.)

For stack or vent shown on block diagram by letter E.

1. Stack height 60 Ft.
2. Stack diameter 3 Ft.
3. Gas temperature stack exit 450°F
4. Stack flow *

For stack or vent shown on block diagram by letter ______.

1. Stack height ______
2. Stack diameter ______
3. Gas temperature stack exit ______
4. Stack flow * ______

For stack or vent shown on block diagram by letter ______.

1. Stack height ______
2. Stack diameter ______
3. Gas temperature stack exit ______
4. Stack flow * ______

* See Instructions

VI. Tankage.

No. of tanks	composition	temp.	capacity (each)	approximate turnovers per year	method of vapor conservation
3	Pyrrolidine $(CH_2)_4NH$	Ambient	100,000 gal.(ea)	50	None, vents to air
4	Pyrrole $(CH)_4NH$	Ambient	100,000 gal.(ea)	25	"
1	Pyrrolidone $(CH)_2CH_2CONH$	Ambient	100,000 gal.(ea)	25	"

VII. Fuels.

800,000 gal./year fuel oil for fired air heater 3% sulfur.

VIII. Other emissions.

No other known emissions although minor leakages probably occur.

Engineering estimate of average losses is 0.01% of throughput or 13,000 lbs./year of amines.

IX. Future plans.

1. Current research on heavy amine stream indicates further processing will produce a marketable product - if so, incinerator will be shut down.
2. We are currently negotiating a long term contract to purchase 1% sulfur fuel oil from the Flused Oil Company.

APPENDIX III

FINAL QUESTIONNAIRE SUMMARY

Chemical	Number of Questionnaires used as Basis for Report
Acetaldehyde via Ethylene	1
via Ethanol	1
Acetic Acid via Methanol	2
via Butane	1
via Acetaldehyde	1
Acetic Anhydride	2
Acrylonitrile	4
Adipic Acid	4
Adiponitrile via Butadiene	1
via Adipic Acid	2
Carbon Black	7
Carbon Disulfide	4
Cyclohexanone	7
Dimethyl Terephthalate (+TPA)	6
Ethylene	13
Ethylene Dichloride via Oxychlorination	10
via Direct Chlorination	3
Ethylene Oxide	7
Formaldehyde via Silver Catalyst	12
via Iron Oxide Catalyst	6
Glycerol	2
Hydrogen Cyanide	1
Isocyanates	10
Maleic Anhydride	7
Nylon 6	4
Nylon 6,6	3
Oxo Process	6
Phenol	8
Phthalic Anhydride via o-xylene	5
via naphthalene	3
Polyethylene (High Density)	5
Polyethylene (Low Density)	7
Polypropylene	7
Polystyrene	4
Polyvinyl Chloride	8
Styrene	7
Styrene - Butadiene Rubber	6
Vinyl Acetate via Acetylene	3
via Ethylene	1
Vinyl Chloride	8

INTRODUCTION TO APPENDIX IV AND V

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix IV discussion are:

1. Prediction of numbers of new plants.
2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix V discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX IV

Number of New Plants by 1980

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It is felt that no useful end is served by creating a large number of sub-groupings because it will merely compound the problem of assigning a weighting factor. Therefore, it is proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it is proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical____________________

Process____________________

Increased Capacity________________

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	

Total____________________

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane will be included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. This determination is to be made on the basis of data reported on returned questionnaires.

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It is proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix V
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it is proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It is recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it is recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it is recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\ O_2 \longrightarrow C + 2\ CO + 3\ CO_2 + 6\ H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

$$\text{However, } SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$$

$$\text{and } SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it is suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 95\%$$

and

$$SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

and

$$SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$